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Atmos. Chem. Phys. Discuss., 4, 2167–2238, 2004
www.atmos-chem-phys.org/acpd/4/2167/
SRef-ID: 1680-7375/acpd/2004-4-2167

Atmospheric Chemistry and Physics Discussions

Ozone loss and chlorine activation in the Arctic winters 1991–2003 derived with the TRAC method

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Received: 11 March 2004 – Accepted: 3 April 2004 – Published: 4 May 2004

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Abstract

In this paper chemical ozone loss in the Arctic stratosphere was investigated for twelve years between 1991 and 2003. The accumulated local ozone loss and the column ozone loss were consistently derived mainly on the basis of HALOE observations. The ozone-tracer correlation (TRAC) method is used, where the relation between ozone and a long-lived tracer is considered over the lifetime of the polar vortex. A detailed quantification of uncertainties was performed. This study demonstrates the interaction between meteorology and ozone loss. The correlation between temperature conditions and chlorine activation becomes obvious in the HALOE HCl measurements, as well as the dependence between chlorine activation and ozone loss. Additionally, the degree of homogeneity of ozone loss is shown to depend on the meteorological conditions, as there is a possible influence of horizontal mixing of the air inside a weak polar vortex edge.

Results estimated here are in agreement with the results obtained from other methods. However, there is no sign of very strong ozone losses as deduced from SAOZ for January considering HALOE measurements. In general, strong accumulated ozone loss is found to occur in conjunction with a strong cold vortex containing a large potential area of PSCs, whereas moderate ozone loss is found if the vortex is less strong and moderately warm. Hardly any ozone loss was calculated for very warm winters with small amounts of the area of possible PSC existence (A_{PSC}) during the entire winter. Nevertheless, the analysis of the relationship between A_{PSC} (derived using the PSC threshold temperature) and the accumulated ozone loss indicates that this relationship is not a strictly linear relation. An influence of other factors could be identified. A significant increase of ozone loss (of ≈40 DU) was found due to the different duration of illumination of the polar vortex in different years. Further, the increased burden of aerosols in the atmosphere after the Pinatubo volcanic eruption in 1991 and the location of the cold parts of the vortex in different years may impact the extent of chemical ozone loss.

ACPD

4, 2167–2238, 2004

1. Introduction

The mixing ratio of stratospheric ozone in the Arctic vortex is determined by both chemical reactions and by transport. In particular, the most prominent transport process inside the polar vortex is the diabatic descent of air during winter. Descent of air tends to increase the ozone mixing ratio at a given altitude, because ozone mixing ratios are larger in higher altitudes in the lower stratosphere. Thus, air with large mixing ratios of ozone is transported downwards into the lower stratosphere, the region, where chemical ozone destruction occurs. Ozone variations due to transport are often of the same magnitude as those due to chemical ozone destruction (e.g. Manney et al., 1994; von der Gathen et al., 1995; Müller et al., 1996). Therefore, it is necessary to separate these two processes in order to quantify the chemical ozone loss in the stratosphere.

Different approaches were developed over the last decade to separate transport and chemistry employing the explicit model calculation of diabatic descent (e.g. Rex et al., 1999b; Manney et al., 2003a; Knudsen et al., 1998; Goutail et al., 1999; Lefèvre et al., 1998; Harris et al., 2002). Another possibility in deriving chemical ozone loss, is to exclude transport processes implicit, using the tracer-tracer correlation (TRAC) method (e.g. Proffitt et al., 1990; Müller et al., 1996, 1999, 2002; Tilmes et al., 2003b), as it is used in this study.

Chemical ozone loss in the polar stratosphere is caused beyond doubt by the burden of CFCs in the atmosphere, which is due to anthropogenic emissions (e.g. Solomon, 1999; WMO, 2003). The inactive chlorine reservoir species are converted into active – ozone destroying – form through heterogeneous reactions on the surface of polar stratospheric clouds (PSCs). PSCs form during a cold period of the Arctic winter. Therefore, chemical ozone depletion is linked with meteorological conditions (e.g. Manney et al., 2003a; Rex et al., 2002). Santee et al. (2003) discussed the connection between interanual variability of the ClO abundance and meteorological conditions during the 1990s. The strongest ClO abundance was found in the very cold winter 1995–1996 in the Arctic lower stratosphere.

ACPD
4, 2167–2238, 2004

In this paper, ozone loss was analysed consistently over the period of the last twelve years (1991–1992 to 2002–2003) using the TRAC method, mainly on the basis of Version 19 HALOE satellite observations (Russell et al., 1993). Recent improvements of the method (Müller et al., 2002; Tilmes et al., 2003b) and further enhancements, described in this study, enable a comprehensive error analysis of the derived chemical ozone loss. We present a detailed analysis for each year including the correlation between ozone loss, chlorine activation and the area of possible PSC existence (A_{PSC}).

A comparison is performed between ozone loss derived using the TRAC method and other methods using model simulations to estimate transport processes. Reliable results inside the range of uncertainty during a period of twelve years allow considering the correlation between A_{PSC} and the calculated column ozone loss and accumulated local ozone loss between early winter and spring. The correlation indicates an increase of ozone loss with increasing A_{PSC}. This relation is not a linear correlation. Besides A_{PSC}, here further dependencies of the chemical ozone loss was found. Other factors are controlling chemical ozone loss. The illumination time of solar radiation onto cold parts of the vortex may have significant influence on ozone loss, as well as the loading of volcanic sulfate aerosols in the atmosphere.

2. The tracer-tracer (TRAC) method

2.1. Methodology

The tracer-tracer correlation (TRAC) technique has its seeds in the study of Roach (1962) and later Allam et al. (1981). They first noticed that a relation between two different species arise by the elimination of dynamical variability from measurements. Compact relations between long-lived tracers in the stratosphere were first observed by Ehhalt et al. (1983) and were simulated using various chemical transport models (Mahlman et al., 1986; Holton, 1986; Plumb and Ko, 1992; Avallone and Prather, 1997) and recently by Sankey and Shepherd (2003). Proffitt et al. (1990) first developed

ACPD
4, 2167–2238, 2004

the TRAC technique to quantify chemical ozone loss inside an isolated vortex from high altitude aircraft measurements. Later this technique was applied and extended to satellite (Müller et al., 1996, 1997; Tilmes et al., 2003b) and balloon (Müller et al., 2001; Salawitch et al., 2002) measurements. The TRAC method was further used to investigate chlorine activation (through the analysis of HCl-tracer correlations) (e.g. Müller et al., 1996; Tilmes et al., 2003a) and denitrification (through the analysis of NO_y-N_2O correlations) (e.g. Fahey et al., 1996; Rex et al., 1999a).

Over the course of the winter constant compact relationships are expected for tracers with sufficiently long lifetimes for the air mass inside the polar vortex that is largely isolated from the surrounding air masses (Plumb and Ko, 1992). Therefore, considering relations between two chemically long-lived tracers, the effect of transport can be excluded (e.g. Proffitt et al., 1993). If one of the tracers is subject to chemical or physical change (active tracer), owing to the special meteorological conditions inside the polar vortex, changes in mixing ratio are identified as changes of the tracer-tracer correlation (e.g. Müller et al., 1996, 2002; Tilmes et al., 2003b).

Here, we use the TRAC method to consider the correlation of two long-lived tracers inside the polar vortex during twelve Arctic winter periods. To decide whether profiles are inside or outside the Arctic vortex a methodology is employed based on UKMO meteorological analysis allowing accurate selection criteria (Tilmes et al., 2003b). Three vortex regions are defined, based on the algorithm derived by Nash et al. (1996), the vortex core, the outer vortex (the area between vortex core and vortex edge) and the outer part of the vortex boundary region (outside the vortex edge). Further, trajectory calculations were used to reposition each measured profile to noon. This is the time at which UKMO meteorological analysis are available to apply the Nash et al. (1996) algorithm .

The HALOE instrument (Russell et al., 1993) measures two long-lived tracers, namely CH_4 and HF. Both tracers can be used to calculate chemical ozone loss with the TRAC technique. Additionally, the use of these two long-lived tracers enables a further improved selection criterion for the HALOE profiles. Because CH_4 and HF have very

ACPD
4, 2167–2238, 2004

long lifetimes, the relationship between CH_4 and HF inside the polar vortex region is nearly linear, and does not change significantly over the whole lifetime of the vortex in each year. In this study, a linear relationship from HALOE measurements was derived from profiles inside the polar vortex for each year, with a standard deviation less than 0.1 ppmv (Table 1). Profiles deviating more than 0.2 ppmv from the constant CH_4/HF relation are neglected in order to eliminate observations that are uncertain.

Besides CH_4 and HF, the HALOE instruments measures ozone and HCl, which are used as the active tracers in this study. HCl is chemically destroyed by heterogeneous reactions and increases due to the deactivation of chlorine via the reaction of Cl with CH_4. Chemical ozone loss occurs if large concentrations of chemically active halogen compounds are present in an air mass. This is the case in late winter and spring inside the polar vortex in the presence of sunlight.

To derive chemical losses of ozone, first, the ozone-tracer relation has to be determined at a time before ozone has chemically changed. This is usually the case in the early winter when rather little sunlight is present. The ozone-tracer relation, referred to as "early winter reference function", is mathematically formulated as a polynomical and is considered as the reference for chemically unperturbed conditions. It is necessary to derive an early winter reference function for each of the considered twelve years to determine chemical ozone loss for each year. For this, the observation time of the underlying profiles considered has to be chosen carefully. The turning point from summer to winter circulation marks the time of the formation of the polar vortex. Thus, the time of the minimum of the ozone column density is the earliest time at which the early winter reference function can be determined. This point in time can be derived considering the total ozone column form global satellite measurements. Tilmes (2003, Sect. 3.3) used TOMS observations for this purpose. On the other hand, this time of the winter may be not the most suited time to derive the early early winter reference function, if the early vortex is not yet strong enough. Horizontal mixing across the vortex edge may change the tracer-tracer relation without chemical changes. A case in point is the winter 1996–1997, where the ozone-tracer relation changed until the beginning of Jan-

ACPD
4, 2167–2238, 2004

uary 1997, due to horizontal mixing processes derived from ILAS observations (Tilmes et al., 2003b). Further, in winter 1991–1992 the ozone-tracer relation changed from November 1991 to December 1992 due to mixing derived from HALOE observations.

In summary, the early winter reference function has to be determined at a time when the vortex has already formed and, additionally, is sufficiently isolated from mid-latitude air, but at the same time early enough so that no ozone loss has already taken place. Therefore, if the vortex is isolated, the reference function has to be derived as early as possible, if observations are available, to ensure that no ozone loss has already occurred.

To draw conclusions on possible chlorine activation and therefore possible ozone loss in a certain time period, the consideration of the value of "area of possible PSC existence", A_{PSC}, is useful, because significant chlorine activation is not possible without the existence of PSCs (Solomon, 1999). Significant ozone loss is not possible without the existence of active chlorine components and further, without the present of sunlight.

A_{PSC} describes the total area on a certain potential temperature level, where the temperature (determined from the UKMO analysis) does not exceed the PSC threshold temperature. This PSC threshold temperature was calculated (Hanson and Mauersberger, 1988) for a HNO_3 mixing ratio of 10 ppbv and a H_2O mixing ratio of 5 ppmv. Therefore, if PSC existence is not possible at the time before the early winter reference function was derived, no chlorine activation and ozone loss should have been occurred. On the other hand, an existing potential for PSCs during the early winter may result in active chlorine components that causes ozone loss, if sunlight was present (see below). Using A_{PSC} as an indicator for chlorine activation, it has to keep in mind that these calculations of A_{PSC} do not include these PSCs, which occur on the mesoscale due to orographically induced mountain waves (e.g. Fueglistaler et al., 2003). Further, the use of different meteorological analyses may result in differences up to ≈25% (Knudsen et al., 2002; Manney et al., 2003a). If HALOE measurements are available at the time for which the early winter reference function is determined, chlorine activa-

ACPD
4, 2167–2238, 2004

tion can be clearly detected from the TRAC analysis of HCl-tracer correlations (Müller et al., 1996; Tilmes et al., 2003a) as a strong loss of HCl.

HALOE makes measurements fifteen times per day at each sunrise and sunset occultation along two latitude lines. These lines move between 80° N and 80° S in about 45 days. Therefore, measurements in high northern latitudes are available every two or three months, depending on the year and in most years considered, relatively few observations were available inside the early vortex. Thus, to derive the early winter reference function, additional data sources such as ILAS satellite measurements and balloon measurements were used.

For two out of twelve winters, for which no direct measurements could be obtained in the early vortex, a methodology has been developed to estimate the early winter reference functions. In this way, for each of the twelve winters considered a reliable early winter O_3-tracer reference functions could be derived, as described in Sect. 3.

A reliable calculation of ozone loss during the course of the winter is possible, as long as the polar vortex is isolated well enough, so that the tracer-tracer correlation would remain compact and unaltered in absence of chemical changes. Tilmes et al. (2003b) and Tilmes (2003) have shown that a compact ozone-tracer correlation exists inside the polar vortex during January in the Arctic winter 1996–1997 when no chemical ozone loss is expected due to the lack of sunlight based on ILAS observations. The ILAS instrument measured seven month in high northern latitudes (58° N–73° N), thus well inside the Arctic vortex most of the time. In these studies it was shown that the vortex has to be isolated well enough to obtain a compact reliable reference correlation. In the winter 1996–1997 this situation was found for the Arctic vortex since January 1997. Further, during winter and spring and exact criterion has to be defined to decide, whether profiles are measured in or outside the vortex, because the characteristics of air outside the vortex is very different to vortex air. Using a mixture of profiles measured in and outside the vortex will lead to the erroneous conclusion that compact ozone-tracer correlation does not exist.

Khosrawi et al. (2004) discussed the evolution of O_3/N_2O of different isentropic levels

based on ILAS measurements. They have not separated isentropic levels at different altitudes into measurements inside and outside the vortex and therfore obtain no compact January relationship, whereas exactly the same data indicate a compact O_3/N_2O correlation inside the vortex core if sorted according Tilmes (2003) (Fig. 4.4, the poleward edge of the vortex boundary region, using the algorithm derived by Nash et al., 1996).

In the study by Sankey and Shepherd (2003) O_3/CH_4 correlation are considered the course of an Arctic winter analysing results of the CMAN model. The ozone-tracer correlations on the different isentropic levels are similar to those shown by Khosrawi et al. (2004). Thus the shape of the lines should not be seen as a lack of compactness inside the polar vortex, as it is interpreted by Sankey and Shepherd (2003), but it is rather the result of considering measurements in high northern latitudes, which are not separated in profiles measured outside and inside the polar vortex.

Further, Müller et al. (2001), used balloon-borne measurements in the Arctic winter 1991–1992 to show that the impact of mixing between air masses from outside the vortex with air inside the vortex would result in a tendency to greater ozone mixing ratios in the ozone-tracer relation. Recent model calculations for the development of tracer distributions in the winter 1999/2000 (Konopka et al., 2003) corroborate this finding. The effect should thus lead to an underestimation of the chemical ozone loss. Tilmes et al. (2003b) have shown that this effect is not significant since January 1997 using ILAS observations. Even inside the vortex remnants in May 1997, a compact correlation is found.

In this study we argue that a compact correlation exists during all the observed twelve Arctic winters. Especially, the analysis of the very warm winters (1998–1999 and 2001–2002) – where no substantial chemical ozone loss is expected – demonstrates that the ozone-tracer correlations do not significantly change due to mixing processes, although the vortices are less strong compared to other winters. Only if the vortex totally breaks down and reforms, as it was the case in March 2001, no reliable results can be obtained using the TRAC technique.

ACPD
4, 2167–2238, 2004

2.2. Error analysis

An error analysis was consistently performed for all the years analysed here. In the early winter and during the course of the winter, the scatter of the ozone-tracer relations arises, on the one hand, due to variability of the mixing ratios of tracers inside the vortex, and, on the other hand, it may possibly be due to the random error of the satellite measurements. Both these uncertainties are estimated with the calculation of the standard deviation of the profiles contributing to the early winter reference function.

Further, any systematic error of the satellite measurements is not taken into account, because assuming that all available measurements of one satellite are affected in the same way it would have no impact on the ozone loss calculation. Therefore, the uncertainty of results was derived from the uncertainty of the early winter reference function. Additionally, the standard deviation of monthly averaged column ozone loss deduced from the individual profiles is considered. It describes the homogeneity of the deduced ozone loss during a particular time span and in a particular region. Inhomogeneities may be caused by both, the inhomogeneity of the ozone loss inside the vortex, and, the random error of the satellite measurements, as described above.

To derive results with minimum uncertainty, it is also necessary to calculate ozone loss in the appropriate altitude range. Column ozone loss is therefore calculated for an altitude range of 380–550 K, 400–500 K and 380–600 K (to compare the results with other studies) from HALOE observations, because within this range the empirical ozone-tracer reference relations are valid and possible mixing processes below 380 K are excluded. The smallest uncertainty arises if the column ozone loss is calculated in an altitude range between 400–500 K. Here, the vortex is most compact and accuracies of observation data are better than at lower altitudes.

ACPD
4, 2167–2238, 2004

3. Ozone-tracer and HCl-tracer relations and PSC area

3.1. Development of early winter reference functions

The early winter reference functions is derived from all available HALOE measurements inside the early vortex for the six winters 1992–1993 to 1995–1996 and in 1998–1999 and 2001–2002. The profiles used were located inside the early vortex for each year, at a time when in general no ozone loss was expected (as outlined below). In 1991–1992 (Müller et al., 2001), 1999–2000 (Müller et al., 2002) and 2002–2003 (Tilmes et al., 2003a), early winter reference functions were derived from balloon observations. In winter 1996–1997 ILAS observations were used to define an early winter reference function to calculate ozone loss from measurements made by HALOE (Tilmes et al., 2003b).

An overview of the mathematically formulated tracer-tracer early winter reference functions derived from HALOE observations only inside the early vortex is summarised in Tables 2 and 3. As in Table 1, polynomial functions of the form: $[y]= \sum_{i=0}^{n} a_i \cdot [x]^i$ with $n \leq 4$ are reported as well as the standard deviation of the observation points from the fitted reference function σ. The empirical relations are valid for mixing ratios of CH_4 in ppmv, HF in ppbv and O_3 in ppmv, respectively.

As an example, the derivation of the early winter reference function in 1995–1996 from HALOE profiles inside the early vortex is discussed. In this winter HALOE vortex profiles were available at the end of November. At this time of the winter, the A_{PSC} was negligible. No deviation from the unperturbed HCl/HF relation was found. Therefore, no activated chlorine compounds and thus no ozone loss can be expected. At the end of January (Fig. 1, bottom panel) one profile inside the vortex boundary region indicates strong chlorine activation noticeable as a change in the HCl/HF relation in correspondence which a large A_{PSC} during January. But still, no changes in the O_3/HF relation are detected (Fig. 1, top panel). Changes in the O_3/HF relation due to isentropic mixing are not expected during December and January, because at that time the vortex was already very strong. Therefore, this single January profile still describes the chem-

ACPD
4, 2167–2238, 2004

ically undisturbed O_3/HF relation. Of course, the HCl-tracer relation decreases much faster than the O_3-tracer relation, because chlorine activation occurs on much shorter time scales than ozone loss. However, in this winter ozone loss causes deviation from the derived early winter reference function that is less than its range of uncertainty. The fact that in 1996 – in spite of the early vortex having been cold and strong – no significant ozone loss occurred during January may be explained by the very small amount of sunlight that has illuminated the early vortex. The delayed occurrence between chlorine activation and ozone loss is further discussed below, considering the tracer-tracer correlation during spring.

In the following, the derivation of the early winter reference function from balloon observations in 1991–1992, 1999–2000 and 2002–2003 is briefly described. For winter 1991–1992, the early winter reference function was derived from measurements of ozone and N_2O made by cryosampler measurements (Schmidt et al., 1987) on 5 and 12 December 1991, respectively. The O_3/N_2O profiles were transformed to O_3/CH_4 with the N_2O/CH_4 relationship from Engel et al. (1996), see Müller et al. (2001). To derive the O_3/HF reference function the O_3/CH_4 relation was converted using the CH_4/HF relation derived from HALOE observations for the winter 1991–1992 (Table 1).

The vortex started forming in November 1991. One HALOE profile was found inside the early vortex at the beginning of November, with low ozone mixing ratios compared to profiles inside the vortex measured in January (see Fig. 2, black asterisks). At that time the vortex was not well developed and mixing in of air masses from outside the early vortex was still possible. Therefore, the low ozone mixing ratios observed in November increased until the vortex became fully isolated in December. The HALOE profiles in January 1992 scatters below the derived reference relation for about 1.2 ppmv (see Fig. 2). Thus ozone loss have already occurred during January 1992, corresponding to a small detected area of possible PSC existence at the beginning of January (see Fig. 6). In contrast to the winter 1995–1996, ozone loss during January 1992 was much stronger although A_{PSC} in January 1995–1996 was even larger than in January 1991–1992. This shows that ozone loss is influenced by more than A_{PSC} as

ACPD
4, 2167–2238, 2004

further discussed in Sect. 6.

In winter 1999–2000 again no HALOE observations were available inside the early vortex to derive the early winter reference function. Fortunately, during the SOLVE-THESEO 2000 campaign two balloon flights were conducted inside the early vortex, the OMS (Observations of the Middle Stratosphere) in-situ flight on 19 November 1999 and the OMS remote flight on 3 December 1999 (Müller et al., 2002). HF measurements were only available from the MkIV instrument on the OMS-remote flight. Thus, these data were used to derive the O_3/HF reference function for this winter. Two early winter reference functions were derived using CH_4 as the long-lived tracer, one was derived using the OMS-in-situ measurements and the second using the OMS-remote flight measurements (Müller et al., 2002). For 2002–2003, MkIV balloon observations in mid-December 2002 (Toon et al., 1999) were used to derive the early winter reference function (Tilmes et al., 2003a).

The early winter reference functions of the winters 1994–1995 and 2002–2003 were derived from measurements at a time, when the vortex was already developed. Before this time, a large area of PSCs was already detected and some activation of chlorine already occurred (Tilmes et al., 2003a). HALOE measurements in January 1994–1995, show strong deviations of the HCl/HF relations at the time when the reference function was deduced. Rex et al. (2003b) and Goutail et al. (1999) reported large ozone loss rates for January 1995. These losses may have already result in a small decrease of the O_3/HF relation before the reference function was deduced. Therefore, these ozone losses cannot be included in the calculations below.

The derived ozone-tracer early winter reference functions for ten out of twelve years are shown in Fig. 3.

The ozone-tracer relation in the early winter has its own characteristics each year, mainly due to inter-annual differences in polar vortex development and not due to chemical loss (Manney et al., 2003b). Thus, it is not possible to use one single reference function for all years. Year to year variations are also possible due to the changes of mixing ratios of the long-lived tracer used. Especially the increase of HF from 1991

ACPD
4, 2167–2238, 2004

to 2003 should have an influence on the O_3/HF reference function.

Therefore, two early winter reference functions, one for winter 1997–1998 and another for 2000–2001, were constructed from a climatology of all HALOE profiles that were measured inside the early vortex over the ten year period between 1992 and 2002. Actually, measurements inside the early vortex are available for six winters (1992–1993, 1993–1994, 1994–1995, 1995–1996, 1998–1999 and 2001–2002). The HALOE O_3/HF and O_3/CH_4 profiles are corrected for the growth rate of HF and CH_4, respectively, between each single year and the year 1997–1998 (2000–2001). The CH_4 growth was taken from the tropospheric growth rate derived by Simpson et al. (2002). The HF growth rate was deduced from the HALOE HF/CH_4 relationships (Table 1) (Tilmes, 2003). No correction was applied to ozone, because ozone was relatively constant during the 1990s in northern latitudes (WMO, 2003). The O_3/CH_4 and O_3/HF profiles inside the early vortex of the six years transformed in this way are used to construct reference functions for 1997–1998 and 2000–2001 determined from all available HALOE measurements inside the early vortex. Thus, for the winter 1997–1998 and 2000–2001 in each case two early winter reference relations were derived, one using HF as the long-lived tracer and one using CH_4 (Tables 2 and 3).

3.2. Tracer-tracer development during twelve Arctic winters

Active chlorine inside the polar vortex causes chemical ozone loss. Chlorine activation in the Arctic lower stratosphere may be identified as a strong reduction of HCl compared to normal values. Therefore, using measurements made by HALOE, the evolution of the chlorine chemistry can be inferred from the development of the HCl-tracer relation during each year. The evolution of HCl-tracer relation and O_3-tracer relation is analysed for each of the twelve observed winter periods (Figs. 4 and 5). The temperatures thus control the activation of chlorine and consequently the chemical destruction of ozone. If temperatures are sufficiently low PSCs can occur in the polar stratosphere. Therefore, A_{PSC} is used here to analyse the interaction between meteorology and development of tracer-tracer relationship for each winter (Fig. 6). Further, a division into

cold, moderately cold and warm winters is carried out.

– 1991–1992:
The cold vortex in winter 1991–1992 was disturbed by several warming pulses between November and February (Naujokat et al., 1992). The threshold temperature for PSCs was only reached during January. Therefore, significant ozone depletion can be expected starting in January 1992. During March the temperatures at the north pole steadily increased and the vortex finally broke down at the end of April (Naujokat et al., 1992). In February and at the beginning of March very low HCl mixing ratios are clearly noticeable and strong chlorine activation (Fig. 4) occurred in the lower stratosphere (below ≈420 K).

By April, the HCl levels have increased towards unperturbed values, especially in altitudes below ≈420 K. The vortex became steadily weaker during April. From February up to the beginning of April a homogeneous moderate deviation from O_3/HF reference functions was occurring.

– 1992–1993:
The vortex in winter 1992–1993 was cold and nearly undisturbed until the end of January. A strong minor warming in February shifted the cold air (with low ozone values) towards Europe. This, together with a blocking anticyclone in the troposphere, led to low total ozone values over Europe in February (Naujokat and Labitzke, 1993). Conditions for chemical ozone loss were reached, because of the low stratospheric temperatures (Fig. 6). Unfortunately, no measurements were taken inside the vortex in February, but HCl measurements inside the outer part of the vortex boundary region indicate a strong chlorine activation in February at lower altitudes (Fig. 4, small green crosses). Temperatures started rising in March and the final break-up of the vortex occurred around 10 April. At that time HCl levels have recovered to unperturbed values. Strong (homogeneous) deviation from the O_3-tracer reference function is obvious in March and April (Fig. 5). Until the end of April, the deviation from the O_3/HF reference function does not further

change inside the remaining parts of the vortex.

– 1993–1994:
The early vortex in winter 1993–1994 was slightly disturbed in November, December and January (Naujokat et al., 1995a). Owing to the warming over Europe in February, the vortex was split most of the time. At the end of February and the beginning of March, the vortex air masses cooled down again and temperatures were below the threshold for the existence of PSCs for a few days (Fig. 6). A small decrease of HCl in February is noticeable from the HCl/HF relation (Fig. 4). Afterwards HCl strongly decreased during March (HCl mixing ratios were below 0.1 ppbv for HF mixing ratios below 0.7 ppbv). During April the HCl levels quickly increased while the vortex became weaker. In March and April moderate deviations from the O_3/HF reference function became noticeable (Fig. 4), although the chlorine activation in March seemed to be quiet pronounced.

– 1994–1995:
The vortex in 1994–1995 formed early and was very cold and strong especially between mid-December and mid-January. A large A_{PSC} was deduced for the whole of January 1995. Owing to a warming event in February the vortex was displaced towards Siberia but did not break. The temperatures of the cold centre of the vortex towards Siberia were low enough for PSC formation until 10 February (Naujokat et al., 1995b). Record low temperatures were reached again in the lower stratosphere in March (Naujokat et al., 1995b). In April the vortex split and one part rapidly weakened and disintegrated over eastern Asia. The main vortex centre vanished more slowly. As in winter 1992–1993, a strong decrease of HCl mixing ratio in the outer part of the vortex boundary region was observed by HALOE in February. Although the chlorine activation in March was not as strong as in the previous winter 1993–1994, much stronger deviations from the O_3-tracer reference relation in March were observed. During April the HCl levels have increased towards unperturbed values.

ACPD
4, 2167–2238, 2004

– 1995–1996:
The winter 1995–1996 was the coldest recorded by the US National Meteorology Center (NMC) in 18 years (Manney et al., 1996). Since December 1995, the stratospheric temperatures in the Arctic were below the PSC threshold until March. The final warming began in early March. Measurements taken by HALOE in the vortex are available for the first part of March and the first part of April. The strongest chlorine activation in March for this twelve-year overview was observed. In April, HCl levels have almost completely recovered to unperturbed values. The deviation from the early winter reference function O_3/HF is the same for March and April, so that in April no further ozone loss was identified between March and April.

– 1996–1997:
In winter 1996–1997, the polar vortex formed in November. It was strongly disturbed at the end of November and reformed again during December. Before the vortex was fully established at the end of December, horizontal mixing between air from inside and outside the vortex occurred and the minimum temperature remained above the PSC threshold of ≈195 K. After the reformation, the vortex was very cold and strong. At the 475 K potential temperature level, the lowest temperatures in an 18-year data set were reached in this year in March and April (temperatures were below the PSC threshold until the beginning of April) inside the vortex core (Coy et al., 1997). In March, the vortex core was small and strong whereas the boundary region was wide. PSC occurrence was not possible before January therefore no chlorine activation and thus no ozone loss can be expected in November and December 1996. Until the end of March the temperatures were low enough for PSC existence (Fig. 6). During mid-February, this potential for chemical ozone loss was enhanced by significant denitrification (Kondo et al., 2000). Deviations from the O_3-tracer early winter reference function are separated into two parts. The chlorine activation is also rather inhomogeneous with the strongest decrease of HCl inside the vortex core, except for one profile inside

ACPD
4, 2167–2238, 2004

the outer vortex, measured in the second part of March (Fig. 4, small purple plus sign). The strongest April decrease of HCl mixing ratio was observed in this year, because the vortex remained intact for an extremely long period.

– 1997–1998:
The vortex in 1997–1998 was slightly disturbed throughout the whole winter. The final warming began in the middle of March (Pawson and Naujokat, 1999). Minimum temperatures were low enough to activate HCl during December and during January (Fig. 6). Moderate chlorine activation was observed by HALOE in March and only small deviations from the reference function for O_3-tracer occurred. In that winter HALOE data are only available for March inside the polar vortex.

– 1998–1999:
The winter 1998–1998 was unusually warm due to a major stratospheric warming in mid-December (Manney et al., 1999). The vortex in 1998–1999 was very weak and disturbed. Almost no changes in the HCl/HF relation occurred, owing to a small A_{PSC} and thus, very little chlorine activation at the end of February. However, small deviations from the O_3/HF early winter reference function were found (see discussion below).

– 1999–2000:
In 1999–2000 the Arctic stratosphere was very cold from the middle of November to late March (Manney and Sabutis, 2000). The lowest values of the February HCl mixing ratios for any of the observed years were reached, owing to the largest A_{PSC} during January in the observed period. HCl mixing ratios are comparable to the low mixing ratios in March 1996. In March 2000, a slight recovery of HCl levels towards unperturbed values became noticeable, with a total recovery at the end of April. The small deviation from the early winter reference function HF/O_3 in February strongly increased in March up to April.

– 2000–2001:

ACPD
4, 2167–2238, 2004

The vortex in 2000–2001 developed during October and November 2000. A strong Canadian warming at the end of November greatly disturbed the vortex. An undisturbed cold period followed from late December until mid-January. Afterwards, a major warming broke down the vortex in mid-February. During this warming, the vortex drifted over central Europe for a few days and PSC conditions were reached due to a short-term cooling of the vortex. The vortex re-established in March and lasted until April. Figure 4 displays strong chlorine activation in February 2001. From March to April HCl levels totally recovered towards normal values. In the ozone-tracer relation in February 2001 one profile inside the outer vortex indicates a significant deviation from the early winter reference function. In March and April the early winter reference function is certainly not valid any more, owing to the temporary break-up of the vortex in February, and ozone-tracer profiles scatter above the derived function. Therefore, the TRAC technique cannot be applied to ozone-tracer profiles in March and April.

– 2001–2002:
The winter 2001–2002 was a very warm winter. Although the temperatures at the end of November reached a record minimum for the period 1979–2001, a strong warming in the second half of December occurred so that the vortex significantly weakened. After the vortex was re-established in January, it was weak and warm until it broke down in May. Very little chlorine activation is noticeable at the end of March 2002 (Fig. 4) and very little deviation from the O_3/HF early winter reference relation is apparent at the end of April.

– 2002–2003:
In this winter the polar vortex formed in November 2002. It was characterised by very low temperatures in the early vortex and chlorine activation already in mid-December 2002. A_{PSC} was largest in December for the entire lifetime of the vortex. Afterwards, temperatures increased around mid-January and the vortex split two times, once in January and once in February. Only a small A_{PSC} was

ACPD
4, 2167–2238, 2004

derived for the following month. Some chlorine deactivation was deduced from the HALOE measurements in the vortex in February. In April, HCl had recovered, thus chlorine was completely deactivated. The strongest deviation from the ozone-tracer reference appeared for the profiles in February, and for one profile in April. A detailed analysis of this winter using the TRAC method is described in (Tilmes et al., 2003a).

To summarise the temperature conditions for winters between 1991–1992 and 2002–2003, five winters are characterised as being cold (1992–1993, 1994–1995, 1995–1996, 1996–1997 and 1999–2000). These winters show a strong decrease of the HCl mixing ratio in the HCl/HF relation in spring and strong deviations of O_3-tracer profiles from the early winter reference function. For the cold winters the daily A_{PSC} average in 400–500 K between January and March is above $3*10^6$ km^2 (shown below in Sect. 6). Moderate deviations from the O_3/HF reference were found in 1991–1992, 1993–1994, 1997–1998, 2000–2001 and 2002–2003. These winters indicating a more frequently disturbed vortex are characterised as moderately cold. The daily A_{PSC} average is ≈1–$2*10^6$ km^2. The winters 1998–1999 and 2001–2002 are warm with very little chlorine activation and very little deviation from the early winter ozone-tracer reference function. The value of the daily A_{PSC} average does not exceed $0.5*10^6$ km^2 for these very warm winters.

4. Ozone loss profiles and column ozone loss

The chemical ozone loss calculated using the TRAC method should be interpreted as the total amount of destroyed ozone in a period between the time of the early winter reference function and the time of the investigated profile. In this section, calculated local ozone loss profiles in February/March each year are presented, as well as the monthly average column ozone loss over the course of the entire winter for two different altitude ranges.

ACPD
4, 2167–2238, 2004

4.1. Vertical ozone loss profiles

For each year, the ozone loss profiles differ with respect to the altitude range where ozone loss occurs, the maximum local ozone loss, the altitude where this maximum loss occurs and the extent of homogeneity of the distribution inside the vortex. Vertical ozone loss profiles are calculated using both HF (Fig. 7) and CH_4 (Fig. 8) as the chemically long-lived tracers. These ozone loss profiles (black symbols) are calculated as the difference between the actually measured ozone concentration O_3 (red symbols) and the corresponding ozone proxy $\hat{O}_3$ (green symbols) (e.g. Müller et al., 1996; Tilmes, 2003).

In all winters considered, significant ozone loss arose mainly in an altitude range between 380 and 550 K. At altitudes below 380 K the uncertainty of calculated ozone loss profiles increased in most winters, because of the increasing dynamic variability, that is the influence of mixing processes.

The amount of ozone destroyed at different altitudes and, therefore, the shape of the vertical ozone loss profiles depends on the different meteorological conditions inside the polar vortex for each winter. The maximum of the vertical ozone loss profile (in mixing ratio) and the corresponding altitude range (in potential temperature) is shown in Table 4 for March (or February in the year 2001 and 2003) of each year.

The results derived using two different tracers are within the combined uncertainties for each year. To perform a comparison between the different years, the average of the maximum ozone loss of the two different long-lived tracers is calculated (Table 4, column 6). The strongest local ozone loss of all the years considered, about 2.4 ppmv in 1995–1996 and 2.5 ppmv 1996–1997, was found in the altitude range from about 450–490 K. In the cold winters of 1994–1995 and of 1999–2000 the maximum of local ozone loss profiles was similarly strong in the altitude range from about 410–460 K. In March 1992 and 1993 local ozone loss is also rather strong, 2.0 ppmv in 1992 and 2.2 ppmv in 1993 at very low altitudes in 390–460 K. Winters termed moderately cold, in the section above, 1991-1992, 1993-1994, 1997-1998 and 2001–2002, show local

ACPD
4, 2167–2238, 2004

ozone loss of about 1.5 ppmv, except for the winter 1991-1992. (The reason for the relatively strong ozone loss in 1991–1992 is discussed below). In 2000–2001 local ozone loss reached 1.7 ppmv from profiles inside the outer vortex in February only, whereas the local ozone loss profiles inside the vortex core did not exceed 1.0 ppmv in February 2000–2001 (Fig. 7). In the warm winters, 1998–1999 and 2001–2002, the local ozone loss is 1.0 ppmv and 0.4 ppmv, respectively.

As well as the value of the maximum itself, the altitude ranges and the width of the peak of the maximum ozone loss differs from winter to winter in correspondence to the location of A_{PSC} during the winter. These factors control the amount of column ozone loss calculated by the vertical integration of the ozone loss profile.

In some years 1991–1992, 1992–1993, 1999–2000, 2002–2003, the ozone loss profiles taken inside the vortex core are very homogeneous (Fig. 8). This is the result of an isolated vortex core with homogeneous ozone loss.

For 1993–1994, 1994–1995, 1995–1996 and 1997–1998, a few profiles of ozone loss indicate a somewhat smaller deviation from the reference function inside the vortex core but the majority of profiles inside the vortex core are homogeneously distributed. In 1993–1994 and 1994–1995 a warming in February disturbed the isolated vortex. The vortex shifted off the pole and the cold region was near the edge of the vortex. At this time rapid ozone destruction occurred at the vortex edge (Manney et al., 2003a). The vortex in 1995–1996 and 1997–1998 was already weakening at the end of February and broke down in March. The ozone loss profiles ΔO_3 in 1996–1997 are separated in two distinct parts with moderate loss inside the entire vortex and strong loss in the vortex core (Tilmes et al., 2003b).

The meteorological developments during various winters, described above, may be responsible for inhomogeneous temperature distributions inside the vortex and, therefore, are responsible for the inhomogeneities in ozone destruction inside the entire vortex. For for the most years considered here, the calculated ozone loss profiles for the outer vortex (plus signs in Figs. 7 and 8) show less ozone loss than the profiles in the vortex core. The temperatures inside the outer vortex are generally not as low as

ACPD
4, 2167–2238, 2004

inside the vortex core and, therefore, less ozone loss occurred inside the outer vortex than inside the vortex core. In some years (March 1994–1995, 1997–1998, 1998–1999 and February 2000–2001) very few profiles show slightly stronger deviations from the reference relation and, therefore, stronger ozone loss inside the outer vortex than inside the vortex core. This is possible, because the exposure to sunlight may be longer inside the outer vortex than inside the vortex core, due to the location of the outer vortex more towards lower latitudes. Further discussion of the differences between ozone loss inside the vortex core and the outer vortex is given below in the next section.

4.2. Column ozone loss

Column ozone loss for a twelve years period was derived by integrating the vertical ozone loss profiles (see Appendix A). This value constitutes a good approximation of the total amount of ozone loss over the entire column of ozone if the vertical integration is extended over a sufficiently large vertical range (≈380–550 K). In this paper, the monthly average column ozone loss is analysed for altitude ranges between 380 and 550 K and between 400–500 K. Further, a comparison of results of different parts of the polar vortex was performed as well as comparison between the results using different long-lived tracers.

Tables 5 and 6 summarise the column ozone loss in 380–550 K and in 400–500 K, respectively, averaged over different months, February, March, April and May (May only in winter 1996–1997), calculated for each year if measurements are available. In February 2000–2001, for two of three profiles measured inside the entire vortex ozone loss was found only in altitudes above ≈450 K (Figs. 7 and 8). These two profiles scatter above the estimated early winter reference function in altitudes below 450 K and would wrongly increase the calculated ozone loss. Thus, for this winter the column ozone loss was calculated for the altitude range between 450 and 500 K only. In Fig. 9 results for the entire vortex are shown, calculated for the altitude range of 380–550 K. The uncertainty of the mean column ozone loss is described by two parameters. The uncertainty which arises solely due to the uncertainty of the early winter reference

ACPD
4, 2167–2238, 2004

function is shown as a red error bar in Fig. 9. The standard deviation of the column ozone loss deduced from the individual profiles, is shown as a black error bar.

The uncertainty of the early winter reference function is about 15–25 DU in the altitude range of 380–550 K (Table 5) depending on the scatter of profiles inside the early vortex from which the reference function was derived. If there is little variability of the mixing ratios of tracers inside the early vortex, the error in the results is smaller than 10 DU. This is the case in the year 1995–1996 using HF as the long-lived tracer and in 1998–1999 using CH_4 as the long-lived tracer. Differences of the uncertainties of the results derived using two different long-lived tracers in one year is possible, due to differences in the random error of the different tracers used. If the early winter reference function was derived using only one profile, as it is the case in 1999–2000 and 2001–2002, information about the variability of the mixing ratios of tracers inside the early vortex are not included, and the estimated error may be underestimated.

For March 1997 the standard deviation of averaged column ozone loss is larger compared to the other winters and is much larger than the early winter reference error (Fig. 9). At this time, the vortex is divided into two parts, a part with strong ozone loss and a part with moderate ozone loss (McKenna et al., 2002; Tilmes et al., 2003b). The ozone loss in March 1996–1997 is spatially much more inhomogeneous than the ozone loss observed in all the other winters investigated here (Fig. 7).

The error which arises owing to the early winter reference function is significantly smaller in an altitude range of 400–500 K than in 380–550 K (Tables 5 and 6). Here, calculated ozone loss for the cold, moderately cold and warm winters between the 400–500 K level is summarised. In the following, the average between the results using CH_4 and HF as the long-lived tracers are considered. In 1992–1993, 1994–1995, 1995–1996 and 1999–2000 column ozone loss is 60–80 DU between the 400–500 K level. The maximum of the column ozone loss in this twelve-year study was obtained for the winters 1992–1993 and 1995–1996. In 1996–1997 the strongest mean ozone loss was reached in May (48 DU in the 400–500 K level). Although the winter 1996–1997 was cold, the mean column ozone loss for this winter (47±17 DU inside the vortex

ACPD
4, 2167–2238, 2004

core in the 400–500 K level in April) is comparable with the results of the moderate winters, because of the inhomogeneity of the ozone loss in the vortex. Nonetheless, the maximum ozone loss locally of this winter is comparable with results of the cold winters (Fig. 7) .

The moderately cold winters 1991–1992, 1994–1995,1997–1998 and 2002–2003 reach a mean column ozone loss between 31 DU (in winter 1994–1995) and 57 DU (in winter 1991–1992) inside the vortex core in March. (Results of winter 2002–2003 using CH_4 as the long-lived tracer are excluded, due to uncertain data, as discussed below). In 2000–2001, mean column ozone loss was deduced for February in 450–500 K, as described above. Only 10 DU were calculated for the entire vortex. Nevertheless, the maximum column ozone loss reached 20±4 DU and 21±6 DU using HF and CH_4 as the long-lived tracers for one profile inside the outer vortex in 450–500 K. In the warm winter 1998–1999 ozone loss still reaches 25±10 DU derived for an altitude range of 400–500 K from profiles inside the entire vortex and 21±10 DU for profiles inside the vortex core. Inside the entire vortex in March 2002 no ozone loss is diagnosed with the TRAC technique within the uncertainty of the early winter reference function.

The exact mean calculated column ozone loss differs depending on whether HF or CH_4 is used as the long-lived tracer. Further, ozone loss differs depending whether the vortex core or the entire vortex is considered. In Fig. 10, the difference between the ozone loss derived with the two long-lived tracers are shown.

The differences between the results are ≈10–20 DU for most of the observed years and are similar for the entire vortex and the vortex core (not shown). The smallest differences are calculated for the winter 1996–1997 and 1997–1998 (below 5 DU). The difference of the early winter reference functions using the two different long-lived tracer are mostly responsible for the different results. In most observed years the results obtained using CH_4 as the long-lived tracer agree with those using HF inside the uncertainty introduced by the uncertainty of the reference function.

In some years, ozone loss calculated employing CH_4 as the long-lived tracer has a tendency towards larger ozone loss toward the end of the winter compared to HF

ACPD
4, 2167–2238, 2004

(Fig. 9). Especially in March 1996, the results differ by more than 30 DU for the entire vortex. In winter 2002–2003 results derived using CH_4 as the long-lived tracer are significantly larger (25–30 DU) than using HF during the entire winter period. The CH_4 mixing ratios inside the Arctic vortex at altitudes below about 450 K may be problematic in these years, due to signal saturation problems. Such problems are also discussed for the winter 1999–2000 by Müller et al. (2002) and may be responsible for the differences in 2002–2003 (Tilmes et al., 2003a). Therefore, results derived employing CH_4 as the long-lived tracer are not discussed in Tilmes et al. (2003a). Also, the significant uncertainties in March 1996 may be explained by this problem.

Inside the outer vortex, the mean column ozone loss is in most cases less than inside the vortex core (Fig. 11). The vortex core usually is colder than the outer vortex and, thus, the extent of ozone loss is expected to be stronger, as described above. This effect is very strong for the winters 1991–1992, 1992–1993, 1996–1997, 1999–2000 and 2002–2003. However, in some years the ozone loss is insignificantly greater inside the outer vortex than inside the vortex core (in April 1992, 1994 and 1995, February and March 1999 and February 2001). As discussed above, this is possible because the exposure to solar radiation may be longer inside the outer vortex than inside the vortex core, which causes stronger ozone loss. Further, in some years the standard deviation for profiles in the outer vortex is significantly larger than inside the vortex core (1992–1993, 1994–1995, 1995–1996 and 1999–2000) (see Tables 5 and 6). That is because the ozone loss inside the outer vortex was much more inhomogeneous than in the vortex core in these winters. These inhomogeneities may be caused by inhomogeneous temperature distributions inside the outer vortex.

5. Comparison with ozone loss estimates using different methods

The results deduced here using the TRAC method are compared with published results obtained by different methods for the determination of chemical ozone loss. Chemical ozone loss in the Arctic vortex in the past decade was estimated by a variety of methods

ACPD
4, 2167–2238, 2004

for different winters (Harris et al., 2002; Newman et al., 2002). However, a comparison between the different ozone loss estimates is only meaningful, if the figures compared are determined for exactly the same conditions (Harris et al., 2002).

Column ozone loss from the SAOZ/REPROBUS approach (Goutail et al., 1999; Deniel et al., 1998; Lefèvre et al., 1998), was estimated for a period from December to March/April for the winters 1993–1994 to 2002–2003 (Goutail et al., 2000, 2003). The TRAC technique estimates ozone loss between the time when the reference function was derived and the time when HALOE measurements are available in March/April. The early winter reference function in winter 1993–1994 was derived from observations at the end of November and at the beginning of January. During these two month no ozone loss was found. To compare the results, ozone loss from SAOZ is also considered for the period between January and March 1994. Considering different altitudes had little impact on the total column ozone loss. In this winter, SAOZ estimated ≈10% ozone loss in December (Goutail et al., 2003) and ≈7% between January and March. If an average of 441 DU is taken from the inert tracer simulations in March 1994 (pers. comm., F. Goutail, 2004) 31 DU ozone loss are estimated for the period between January and March 1994 from SAOZ (Table 7), which agrees well with accumulated ozone derived from HALOE measurements using the TRAC technique.

In winter 1994–1995, the early winter reference function was derived in mid-January. Therefore, SAOZ ozone loss is estimated for the time period between mid-January and March (Goutail et al., 2003) (≈21% or 95 DU, where 452 DU is the approximated passive ozone). This result is somewhat greater than derived from HALOE, although inside the range of uncertainty (Table 7). The ozone loss derived using the Match technique (Rex et al., 1998; Schulz et al., 2000) for the same winter but for the time period between 1 January and March 1995, in 370–700 K, is more than 40 DU larger (127±14 DU) than that from HALOE (in 380–550 K). Like SAOZ, the Match technique estimated strong ozone loss during the first two weeks in January. Because the temporal evolution of ozone destruction estimated by SAOZ and Match coincides quiet well (Rex et al., 1998), we assume that about 12% of 36±4% derived by Match occurred

during the first half of January. This results in accumulated ozone loss of 24±4% (108±18 DU) estimated from Match results, which agrees with HALOE results with the range of uncertainty (Table 7).

The early winter winter reference function in 1995–1996 was derived from both November and January profiles. As for 1993–1994 no ozone loss was found during these two month. SAOZ accumulated ozone loss in winter 1995–1996 between mid-January and March is ≈20% (83 DU). This value is in good agreement with HALOE results. For 1996–1997 the result from SAOZ agrees with the largest ozone loss calculated by HALOE inside the vortex core (90–110 DU), but averages do not agree.

In winters 1997–1998 and 1998–1999 results of SAOZ and HALOE data agrees within the considered uncertainty. The estimated ozone loss from SAOZ in winters 1999–2000, 2001–2002 is ≈20 DU larger than derived here from HALOE.

The column ozone loss from UARS microwave limb sounder (MLS) measurements for the winters 1991–1992 to 1997–1998 was calculated for above 100 hPa (Manney et al., 2003a). Therefore, the results are compared with HALOE results for the potential temperature range 400–550 K (Table 8). The results of the two methods agree in so far as, with both techniques, the strongest ozone loss was found for the winters 1995–1996 and 1992–1993. For the winters 1991–1992, 1992–1993, 1994–1995, the ozone losses determined from MLS data are about 10 DU smaller than the lower limit of the uncertainty range of those derived from HALOE data for profiles inside the entire vortex. In 1995–1996 and 1997–1998 MLS results are smaller than those deduced from HALOE, but within the considered uncertainties of the HALOE results. In 1993–1994 values calculated from HALOE observations are insignificantly smaller (6 DU) than calculated from MLS observations inside the entire vortex. For 1996–1997 the average value of the entire vortex is in accordance with the MLS observations.

MLS values of column ozone loss are reported only for the height range above 100 hPa. The column ozone loss between the potential temperature levels 400–550 K deduced here based on HALOE measurements will not exactly correspond to a loss derived for a height range above 100 hPa, and may include some ozone loss at alti-

ACPD
4, 2167–2238, 2004

tudes further below. This might explain the smaller ozone loss values reported for MLS for some years. Further differences will occur if the time intervals considered using both techniques are not exactly the same (Manney et al., 2003a).

In winter 1999–2000 the column ozone loss inside the Arctic was derived from various measurements and different techniques, because an extensive measurement campaign was conducted: SOLVE-THESEO 2000 (Newman et al., 2002). The calculated ozone loss between early January and mid-March by the Match technique is 71±12 DU (Rex et al., 2002). Results from the OMS balloon measurements (Salawitch et al., 2002) were calculated up to 5 March 2000 as 61±14 DU. An extrapolation of the result for 5 March to mid-March (based on Match-derived ozone loss rates (Müller et al., 2002) yielded 84±13 DU. Ozone loss from POAM/REPROBUS was determined as 80 DU in 380–700 K, as reported by Harris et al. (2002). These results agree well with the column ozone loss found in the present work (86±15 DU in 380–550 K inside the vortex core).

Accumulated local losses in the vortex in mixing ratios were estimated at certain altitudes for various time periods and for given subsiding layers of air with the Match technique (Rex et al., 1998; Schulz et al., 2000), from the MLS observations (Manney et al., 2003a) and by Knudsen et al. (1998) using the vortex average approach. The results should be comparable with the accumulated local ozone loss derived with the TRAC technique, if the time interval considered is comparable.

The accumulated chemical ozone loss was calculated from MLS observations for the winters 1991–1992 to 1997–1998 from December/January to the end of February/March at the 465 K and 520 K level (Manney et al., 2003a) (Table 9). Local ozone loss at the 465 K level derived from HALOE data is consistently ≈ 1 ppmv larger than that derived from MLS observations (see Table 9, column 2 and 3). For the 520 K level, the deviations are less strong; the difference is ≈0.3 ppmv. However, the strongest accumulated ozone loss was found in 1995–1996 from both techniques.

For the years 1992, 1995, 1996 and 2000, largely unexplained stratospheric ozone loss rates during January were found, using a combination of data from Match, POAM

ACPD
4, 2167–2238, 2004

II, POAM III and MLS (e.g. Hansen et al., 1997; Becker et al., 1998, 2000; Rex et al., 2003b; Kilbane-Dawe et al., 2001). Here, only a limited assessment of the problem is possible because of the lack of regular sampling of the polar vortex in January by HALOE. Based on HALOE observations, significant ozone loss in January is apparent only in 1991–1992. In 1995–1996, no ozone loss was found inside the vortex boundary region. However, very small ozone losses occurring, for example, in mid-winter and during warm winters cannot be determined with sufficient accuracy with the TRAC method due to a certain uncertainty range of the reference function. No measurements are available in 1994–1995 and 1999–2000 to calculate chemical ozone loss during early winter. The very large ozone loss rates in the early winter 1993–1994, 1994–1995, 1995–1996 and 1997–1998 derived by SAOZ can be neither confirmed nor falsified here due to the lack of observations. However, there is also no sign of such strong ozone losses as deduced from SAOZ for January considering HALOE measurements within the vortex boundary region in 1993–1994 and 1995–1996.

In winter 1996–1997, accumulated ozone loss was estimated in the time period between the end of January and the end of March by the Match technique (1.1 ppmv) and by Knudsen (0.9±0.2 ppmv) at the 455 K potential temperature level (Harris et al., 2002). Such values are approximately in agreement with the moderate ozone loss deduced from ILAS 0.5–1.0 ppmv (±0.2 ppmv) and HALOE 0.9–1.4 ppmv (±0.2 ppmv) at the 475 K level (Tilmes et al., 2003b). Further calculations of ozone loss were performed with the Match technique based on ILAS observations for the winter 1996–1997 (Terao et al., 2002). There, the integrated ozone loss during February and March reached 2.0±0.1 ppmv at 475–529 K levels. This result is in good agreement with the maximum of the ozone loss profile of 2.0±0.3 ppmv derived from ILAS with the TRAC technique in a similar altitude range (Tilmes et al., 2003b).

However, in winter 1996–1997 vortex average losses obtained by different methods are very difficult to compare, because ozone loss inside the vortex was spatially very inhomogeneous (McKenna et al., 2002; Schulz et al., 2000; Tilmes et al., 2003b). Thus, the averages derived will greatly depend on what fraction of the data entering

ACPD
4, 2167–2238, 2004

the average originates from the vortex region showing the stronger ozone loss.

In 1999–2000 HALOE local ozone loss in 430–450 K (2.3±0.2 ppmv) is in good agreement with the accumulated ozone loss in the vortex in mid-March derived by the Match technique (2.0±0.3 ppmv) (Rex et al., 2002). The ozone and the tracer measurements between early January and mid-March 2000 from the ER-2 were used to deduce chemical ozone loss (1.8±0.3 ppmv) (Richard et al., 2001). Ozone loss deduced from POAM III satellite measurements only reached 1.5±0.3 ppmv for mid-March (Hoppel et al., 2002).

The accumulated ozone loss derived using the vortex average approach (Rex et al., 2002) is most similar to the results derived using the TRAC technique, although there are some significant deviations as described below in detail in Sect. 6.

6. Impact of meteorological conditions on ozone loss

Ozone loss is related to the particular meteorological and dynamic conditions of the polar vortex in each year. The twelve-year time series of ozone loss obtained in a consistent manner in this paper allows this question to be addressed in detail. Rex et al. (2002) reported a similar analysis. They investigated the relationship between the accumulated ozone loss in mixing ratios between day 15 and day 85 of a particular year – averaged between 400–500 K – and the total area of possible PSC existence in the Arctic polar vortex during this time period based on meteorological analysis from ECMWF (Fig. 13, top panel, coloured open circles). The ozone loss was calculated with the vortex average approach inferred from measurements of the Arctic ozone sonde network.

Here, the ozone loss profile deduced from the TRAC technique for measurements inside the vortex core, which describes the accumulated ozone loss between January and March, is averaged between the 400–500 K level for each year. Thus, these ozone loss values are comparable with the values deduced from the vortex average approach.

In this study, the area of possible PSC existence was determined from the analysis

from UKMO in the same altitude range as was done by Rex et al. (2002). Some differences arise between A_{PSC} derived from Rex et al. (2002) (Fig. 12, open circles) and in this study (Fig. 12, filled diamonds), owing to different time intervals considered and also possibly owing to the different meteorological analysis used (Manney et al., 2003a).

In Fig. 12, the averaged daily mean A_{PSC} was calculated for different time intervals. The largest A_{PSC} was calculated for January-February for most of the considered years, because it is the coldest time of the year. The figure demonstrates that A_{PSC} may be strongly variable, depending on the considered time interval. Further, the difference between A_{PSC} averaged for different time intervals strongly depends on the year considered. In this study A_{PSC} and accumulated ozone loss, both were derived in the same time interval between January and March.

Rex et al. (2002) reported that A_{PSC} during the lifetime of the vortex correlates well with the derived accumulated ozone loss with the use of the average approach in the years between 1991–1992 and 1999–2000 (Fig. 13, open circles, top panel). Accumulated ozone loss derived with the TRAC method (Fig. 13, filled symbols) show that ozone loss (in ppmv and DU) and A_{PSC} are positively correlated and thus support the results obtained using the vortex average approach. The black lines (Fig. 13, top and bottom panel) describe possible linear relationships between ozone loss in ppmv and DU, respectively, and A_{PSC}. However, the ozone losses deduced with the TRAC method indicate more complicated relations. Significant deviations from the linear relations between accumulated ozone loss and A_{PSC} are obvious.

The value of accumulated column ozone loss in DU and ozone loss anomaly in DU of the winter 2000–2001 was derived for an altitude range of 450–500 only (Figs. 13 and 14 in brackets) and therefore cannot be included in the discussion below.

Besides A_{PSC}, chemical ozone destruction is expected to be influenced by the duration of the exposure to sunlight of the cold vortex regions, because solar radiation is involved in ozone destroying cycles. To separate different factors controlling ozone loss, thus to eliminate the effect of A_{PSC} to ozone depletion, we consider the devia-

ACPD
4, 2167–2238, 2004

tion of ozone loss values from the linear relation between ozone loss and A_{PSC} (black lines in Fig. 13). We will refer to this quantity as "ozone loss anomaly" hereafter. In Fig. 14, the ozone loss anomaly is plotted against sun hours per day. Sun hours per day were averaged between January and February, and between 400–500 K, calculated only for the cold part of the polar vortex (that is only for temperatures below the PSC threshold). A linear relation between the ozone loss anomaly and sun hours per day is obvious considering both the accumulated ozone loss in mixing ratios and the column ozone loss (Fig. 14, black lines). The effect of different duration of illumination onto the cold parts of the polar vortex is very strong. An increase in sun hours per day of 2.2 h may result in an increase of ≈40 DU column ozone loss inside the vortex core, or ≈0.8 averaged ozone loss, respectively, in 400–500 K.

However, the influence of the duration of illumination does not describe the entire deviation from a linear ozone loss to A_{PSC} relation. The ozone anomalies in winters 1991–1992 to 1994–1995 scatter above the derived linear relation in Fig. 14, black line. These anomalies may be caused by the strong increase in background sulphate aerosols, after the major volcanic eruption of Mount Pinatubo on 15 June 1991. Heterogeneous chemical reactions occur on the surface of these particles, which increases the chlorine activation and, therefore, the amount of ozone loss (Solomon, 1999; Dessler, 2000). Indeed the strongest ozone anomaly, more than ≈40 DU (in 400–500 K) is found for winter 1991–1992. Additionally, the ozone anomaly is getting smaller towards 1993–1994.

More recently, Rex et al. (2003a) derived a linear relationship between accumulated ozone loss (derived between mid-December and the end of March using the vortex average approach) and the potential PSC volume (V_{PSC}) over the same time period. The values of A_{PSC} and V_{PSC} approximately differ by a constant factor and are, therefore, in principle comparable. In that study, deviation of the linear relationship are related to the abundance of volcanic aerosols in the Arctic stratosphere. Nevertheless, this influence is much smaller (with a maximum of ≈10 DU for total ozone loss calculated between 14 and 24 km) than derived here.

ACPD
4, 2167–2238, 2004

Here, additionally, there may be other factors found controlling the amount of ozone loss that may cause the ozone anomaly in 1994–1995. In 1994–1995, ozone loss anomaly is stronger than in winter 1993–1994, although it is expected to be less influenced by volcanic aerosols. In 1992–1993 and 1994–1995, strong chlorine activation was observed in the outer part of the vortex boundary region. Further, in these years, the cold part of the polar vortex was moved towards lower latitudes during February. Thus, ozone destruction may be also related to the location of the area of PSCs. Besides the effect of the increasing solar radiation towards lower latitudes on ozone loss, the displacement of the area of PSC towards lower latitudes may activate parts of the vortex that are not yet activated and therefore does further enhance the ozone loss.

The scattering above a derived correlation between ozone loss and A_{PSC} as well as between ozone loss anomaly and sun hours (Figs. 13 and 14) indicate that the different factors described above increases and not decreases chemical ozone loss.

7. Conclusions

The ozone-tracer correlation technique (TRAC) was applied to measurements in the Arctic polar region made by HALOE from 1991–1992 to 2002–2003. The accumulated local ozone loss in 380–550 K, the average in 400–500 K, the maximum of local ozone loss, and the column ozone loss (in 380–550 K) was derived for different months using HALOE observations. A comprehensive error analysis was performed.

Early winter reference functions for the ozone-tracer relation for all winters between 1991–1992 and 2002–2003 could be derived with the TRAC technique. Changes of the ozone-tracer and HCl-tracer relations during the winter and spring are discussed with respect to the different meteorological conditions in each winter. If the temperatures inside the vortex are low enough strong chlorine activation is identified through the very small HCl mixing ratios in the HCl-tracer relation. Available measurements made by the HALOE instrument indicate a strong ozone loss occurring in the weeks following a period of strong chlorine activation. On the other hand, strong chlorine activation

ACPD
4, 2167–2238, 2004

during February and March does not necessarily cause strong ozone destruction. In years when the vortex was weakening and getting warmer (for example in 1993–1994 and 2000–2001) a pronounced chlorine activation in February and March did not result in further ozone destruction and the observed ozone loss is rather small. Thus, ozone loss occurs with a temporal delay to chlorine activation.

With the recovery of chlorine chemistry, as observed for example in April 1991–1992 to 1995–1996, ozone loss comes to a halt. If the vortex or remnants of the vortex are still isolated in April, a deviation from the reference function remains unaltered from the conditions observed earlier in the year inside the vortex (as in 1992–1993, 1995–1996) or if the vortex remnants exist long enough, additional ozone loss may occur due to NO_x chemistry (as in May 1996–1997). The mixing in of air from outside the vortex due to the break-up of the vortex results in a decrease of the deviation from the reference function as observed in 1994–1995.

The TRAC technique also permits the homogeneity of ozone loss inside the vortex to be described for the twelve year period investigated here. For example, in winter 1996–1997 the calculated ozone losses show a strong inhomogeneity of ozone loss inside the entire vortex (Tilmes et al., 2003b).

Very homogeneous distributions of ozone loss inside the vortex core, for example in 1992–1993, 1999–2000 and 2002–2003, indicate that the vortex core was well isolated up to the time when the observations were made and that the meteorological conditions inside the vortex were rather homogeneous. A more inhomogeneous distribution of the temperature inside the entire vortex results in a larger value of standard deviation of the calculated ozone loss. Thus, inhomogeneous ozone loss profiles indicate an inhomogeneous temperature distribution inside the entire vortex. The TRAC method allows a differentiation to be made between ozone loss inside the vortex core and inside the outer vortex.

A major proportion of the uncertainties in the final results result from the uncertainty of this reference function, which arrises owing to the scatter of profiles used and the lack of observations. The time that is chosen to derive the early winter reference func-

ACPD
4, 2167–2238, 2004

tion strongly depends on the availability of observations inside the early vortex. These are, in most years, limited, due to the incomplete temporal coverage of measurement inside high northern latitudes. The smallest error of the determined ozone loss caused by the uncertainty of the reference function is ≈10% in the cold winter 1995–1996 and ≈15% in the cold winter 1999–2000. In the other cold and moderately cold winters, the error is 20–40%. The error for the winters with little ozone loss (1998–1999 and 2000–2001) is about 50%. In winters 2001–2002 the error is even greater than the result of less than 10 DU ozone loss so that the results derived here are compatible with zero ozone loss.

Thus, the very small ozone losses occurring cannot be determined with sufficient accuracy by using the TRAC method. The more reliably the early winter reference function can be derived, owing to the availability of measurements inside the early vortex, and the more ozone is destroyed in the course of the winter, the more certain the calculated ozone loss is. In summary, the application of the TRAC method permits chemical ozone loss to be calculated as a function of the variability of different meteorological conditions inside the range of uncertainty denoted.

A comparison of the results derived with the TRAC technique and the results derived with the techniques using meteorological models to simulate the transport processes in the stratospheric Arctic vortex was performed. The calculated column ozone loss and local accumulated ozone loss determined in the present work are in agreement with the results of previous studies for the cold and undisturbed vortex in winter 1999–2000. The column ozone loss derived from SAOZ/REPROBUS in 1993–1994, 1994–1995, 1995–1996, 1997–1998 and 1998–1999 agrees well with HALOE results within the considered uncertainties, if calculated between January and March. Results of the winters 1996–1997 to 2002 seems to be a bit large. The very strong ozone loss rates calculated from SAOZ during the early winter in December and first part of January were not found using the TRAC method. Further, the unexpected large ozone losses during January in the winters 1995, 1996 and 2000 based on data from Match, POAM II and POAM III and MLS could not be found using the TRAC method. In the other

ACPD
4, 2167–2238, 2004

winters results estimated with the TRAC technique are in principle similar to the results derived from MLS measurements in the altitude range of 400–550 K, although HALOE results are in general larger.

Furthermore, the results of the TRAC method and of the vortex average approach agree best for the winters 1995–1996, 1996–1997, 1999–2000 and 2001–2002. Nevertheless, larger differences occur in winters where other influences than the possible area of PSC occurrence may affect the amount of ozone loss.

Although the reported error estimates, especially for small ozone loss values, are rather large derived using the TRAC method, the TRAC technique has an advantage. Using TRAC we do not need to simulate all the complicated transport processes within a partly strongly disturbed polar vortex, as it has to be done using other methods.

In this study, a positive correlation between chemical ozone loss and the area of possible PSC existence was derived using the TRAC method. This finding is in agreement with Rex et al. (2003a). Besides A_{PSC}, the duration of solar illumination onto very cold parts of the vortex is another important factor controlling chemical ozone loss. The impact of this effect in the twelve year period reaches up to 40 DU in column ozone loss between an altitude range of 400–500 K, and 0.8 ppm accumulated ozone loss in mixing ratios.

Further, a positive correlation between chemical ozone destruction and the content of sulfate aerosols in the atmosphere, caused by the Pinatubo volcanic eruption in 1991 is clearly noticeable.

Appendix A: calculation of column ozone loss

A detailed description of the calculation of ozone loss in the column density is given here. The column density of ozone or "column ozone" in the unit [molecules per cm^2] is the total amount of ozone molecules per area integrated over altitude. Column ozone is usually given in Dobson Unit (DU); one Dobson unit is $2.69*10^{16}$ molecules/cm^2. To obtain the column ozone loss, the difference between the column of measured ozone

ACPD
4, 2167–2238, 2004

(Col_{O_3}) and the column of the corresponding proxy ozone ($Col_{\hat{O}_3}$) has to be calculated (see Sect. 4.1).

$$Col_{O_{3loss}} = Col_{\hat{O}_3} - Col_{O_3}. \quad (1)$$

The number density of ozone $[O_3]$ (and $[\hat{O}_3]$) in molec/cm^3 has to be vertically integrated over a certain altitude range dz (between the geometric heights z_1 and z_2) to obtain the column ozone in units molecules per cm^2.

$$Col_{O_{3loss}} = \int_{z_1}^{z_2} [\hat{O}_3] dz - \int_{z_1}^{z_2} [O_3] dz. \quad (2)$$

$[O_3]$ (and $[\hat{O}_3]$) can be written as the ozone mixing ratio μ_{O_3} ($\mu_{\hat{O}_3}$) multiplied by the number density of air M (in molec/cm^3). Therefore, the column ozone can be calculated as follows:

$$\int_{z_1}^{z_2} [O_3] dz = \int_{z_1}^{z_2} \mu_{O_3} M dz. \quad (3)$$

The transformation to pressure coordinates is performed using $dp = -\rho g * dz$:

$$\int_{z_1}^{z_2} [O_3] dz = \int_{p_2}^{p_1} \frac{1}{g} * \frac{M}{\rho} \mu_{O_3} dp \quad (4)$$

where the acceleration of gravity $g = 9.81$ m/sec^{-2}, ρ = mass density (in g/cm^3) and p = pressure (in hpa).
The ratio of the density of air M and mass density ρ

$$\frac{M(p,T)}{\rho(p,T)} = \frac{N_A}{m_L} = \text{const.} \quad (5)$$

ACPD
4, 2167–2238, 2004

is constant[1], with the Avogadro Number N_A = 6.02205 * 10^{23} molec/mol and the molecular mass of dry air m_L = 29 g/Mol. Therefore,

$$\alpha = \frac{1}{g} * \frac{M}{\rho} = \frac{1}{g} * \frac{N_A}{m_L} \tag{6}$$

$$\alpha = \frac{1}{981} * \frac{6.0225 * 10^{23}}{29} \left[\frac{\text{molec·sec}^2}{\text{cm·g}}\right] \tag{7}$$

$$= 2.116 * 10^{19} \left[\frac{\text{molec·sec}^2}{\text{cm·g}}\right] \tag{8}$$

$$= 2.116 * 10^{22} \left[\frac{\text{molec}}{\text{hpa·cm}^2}\right] \tag{9}$$

and Eq. (4.5) becomes

$$\text{Col}_{O_3} = \alpha * \int_{p_2}^{p_1} \mu_{O_3} dp. \tag{10}$$

The column ozone in a certain altitude range may be expressed in DU:

$$\int_{z_1}^{z_2} [O_3] dz = \frac{\alpha}{2.69 * 10^{16}} * \int_{p_2}^{p_1} \mu_{O_3} dp \tag{11}$$

$$\int_{z_1}^{z_2} [\hat{O}_3] dz = \frac{\alpha}{2.69 * 10^{16}} * \int_{p_2}^{p_1} \mu_{\hat{O}_3} dp. \tag{12}$$

The main uncertainty in calculating the column ozone loss in Dobson units is introduced through the first term on the right hand side of Eq. (1); the uncertainty of $\text{Col}_{\hat{O}_3}$ is largely a consequence of the uncertainty σ of the early winter reference function (see Sect. 3.1).

[1]Because of the ideal gas law, M = (n · N_A)/V = (ρ · N_A) / (RT) and ρ = (n · m_L) / V = (ρ · m_L) / (RT) with Volume V and number of moles n.

ACPD
4, 2167–2238, 2004

Lower stratospheric ozone loss occurs at altitudes between about 350 and 550 K potential temperature (see Figs. 7 and 8). Thus, the calculated loss inside this altitude range is a good estimate of the ozone loss in the total column.

Acknowledgements. We acknowledge all members of the HALOE data processing teams for their work in producing high-quality data set and the UK Meteorological Office for providing meteorological analyses. We are grateful to the contribution of P. Crutzen, who originally suggested the calculation of column ozone loss with the method explained in Appendix A. We thank U. Schmidt for a thorough review of the thesis part of which forms the basis of this paper. Further, we acknowledge D. S. McKenna and M. Riese for helpful comments and discussion.

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Table 1. CH_4/HF reference relations from HALOE observations inside the vortex core: 1991–1992 to 2002–2003.

valid [x]	a_0	a_1	a_2	a_3	a_4	σ
1991–1992						
0.1–1.1	1.83	−2.49	2.72	−3.31	1.63	$9.03 \cdot 10^{-2}$
1992–1993						
0.1–1.3	1.64	−1.71	$7.33 \cdot 10^{-1}$	$-1.91 \cdot 10^{-2}$	$-1.55 \cdot 10^{-1}$	$9.95 \cdot 10^{-2}$
1993–1994						
0.1–1.35	1.85	−2.75	3.70	−3.15	$9.31 \cdot 10^{-1}$	$1.04 \cdot 10^{-1}$
1994–1995						
0.1–1.4	1.76	−2.71	4.18	−3.71	1.10	$8.98 \cdot 10^{-2}$
1995–1996						
0.1–1.5	1.65	−1.16	$1.77 \cdot 10^{-1}$	$-3.63 \cdot 10^{-2}$		$8.11 \cdot 10^{-2}$
1996–1997						
0.1–1.5	1.76	−1.88	2.25	−2.00	$5.87 \cdot 10^{-1}$	$7.92 \cdot 10^{-2}$
1997–1998						
0.1–1.55	1.71	−1.47	$8.75 \cdot 10^{-1}$	$-4.91 \cdot 10^{-1}$	$8.44 \cdot 10^{-2}$	$8.14 \cdot 10^{-2}$
1998–1999						
0.2–1.6	1.98	−3.44	4.84	−3.40	$8.07 \cdot 10^{-1}$	$8.46 \cdot 10^{-2}$
1999–2000						
0.1–1.65	1.72	−1.89	1.53	$-8.55 \cdot 10^{-1}$	$1.73 \cdot 10^{-1}$	$8.67 \cdot 10^{-2}$
2000–2001						
0.1–1.7	2.05	−2.99	4.10	−3.05	$7.54 \cdot 10^{-1}$	$7.27 \cdot 10^{-2}$
2001–2002						
0.1–1.6	1.89	−2.54	2.90	−1.93	$4.40 \cdot 10^{-1}$	$7.39 \cdot 10^{-2}$
2002–2003						
0.1–1.6	1.91	−2.93	3.90	−2.66	0.61	$8.75 \cdot 10^{-2}$

ACPD
4, 2167–2238, 2004

Table 2. O_3/HF reference relations from HALOE observations: 1992–1993 to 2001–2002 (see text).

valid [x]	a_0	a_1	a_2	a_3	a_4	σ
1992–1993						
0.01–1.	$-199.82 \cdot 10^{-2}$	5.93	$1.47 \cdot 10^{1}$	$-3.19 \cdot 10^{1}$	$1.55 \cdot 10^{1}$	$3.46 \cdot 10^{-1}$
1993–1994						
0.01–1.1	$2.60 \cdot 10^{-1}$	3.81	8.16	$-1.27 \cdot 10^{1}$	4.42	$2.49 \cdot 10^{-1}$
1994–1995						
0.01–1.1	$-1.03 \cdot 10^{-1}$	5.80	$-3.04 \cdot 10^{-1}$	−1.73	$4.79 \cdot 10^{-3}$	$3.77 \cdot 10^{-1}$
1995–1996						
0.01–1.0	$-1.70 \cdot 10^{-1}$	7.93	−6.08	1.92		$1.24 \cdot 10^{-1}$
1997–1998						
0.–1.3	$3.66 \cdot 10^{-2}$	5.87	5.91	$-1.35 \cdot 10^{1}$	5.37	$2.89 \cdot 10^{-1}$
1998–1999						
0.01–1.2	$3.30 \cdot 10^{-1}$	3.23	$1.10 \cdot 10^{1}$	$-1.74 \cdot 10^{1}$	6.91	$1.86 \cdot 10^{-1}$
2000–2001						
0.–1.3	$7.27 \cdot 10^{-3}$	$1.36 \cdot 10^{-1}$	$1.50 \cdot 10^{1}$	$-1.60 \cdot 10^{1}$	4.66	$3.02 \cdot 10^{-1}$
2001–2002						
0.1–1.5	$-4.83 \cdot 10^{-1}$	$1.03 \cdot 10^{1}$	$-1.09 \cdot 10^{1}$	4.98	$-7.06 \cdot 10^{-1}$	$1.48 \cdot 10^{-1}$

ACPD
4, 2167–2238, 2004

Table 3. O_3/CH_4 reference relations from HALOE observations: 1992–1993 to 2001–2002 (see text).

valid [x]	a_0	a_1	a_2	a_3	a_4	σ
1992–1993						
0.45–1.65	8.77	$-2.39{\cdot}10^{1}$	$4.51{\cdot}10^{1}$	$-3.59{\cdot}10^{1}$	9.34	$2.31{\cdot}10^{-1}$
1993–1994						
0.4–1.7	4.72	−6.55	$1.73{\cdot}10^{1}$	$-1.75{\cdot}10^{1}$	5.12	$3.09{\cdot}10^{-1}$
1994–1995						
0.45–1.6	4.19	−3.51	$1.14{\cdot}10^{1}$	$-1.38{\cdot}10^{1}$	4.44	$3.56{\cdot}10^{-1}$
1995–1996						
0.6–1.7	−2.98	$2.55{\cdot}10^{1}$	$-3.00{\cdot}10^{1}$	$1.24{\cdot}10^{1}$	−1.68	$3.09{\cdot}10^{-1}$
1997–1998						
0.6–1.7	3.70	−2.09	$1.00{\cdot}10^{1}$	$-1.19{\cdot}10^{1}$	3.55	$4.40{\cdot}10^{-1}$
1998–1999						
0.6–1.7	$4.55{\cdot}10^{-1}$	$1.27{\cdot}10^{1}$	$-1.27{\cdot}10^{1}$	3.11		$1.04524{\cdot}10^{-1}$
2000–2001						
0.6–1.7	5.00	−8.95	$2.14{\cdot}10^{1}$	$-1.92{\cdot}10^{1}$	5.16	$4.43{\cdot}10^{-1}$
2001–2002						
0.6–1.7	4.49	−6.35	$1.36{\cdot}10^{1}$	$-1.26{\cdot}10^{1}$	3.55	$1.85{\cdot}10^{-1}$

ACPD
4, 2167–2238, 2004

Table 4. Maximum of the local accumulated ozone loss in ppmv in March (February in 2001, 2003) for the winters between 1991–1992 and 2002–2003 in the altitude range (in K), where the loss profile reaches a maximum ±0.1 ppmv, is determined employing both the reference relation using HF and CH_4 as the long-lived tracer, respectively, for the HALOE measurements inside the entire vortex, with an uncertainty derived from the uncertainty of the early winter reference function. Additionally, the averages between the maximum derived using HF and CH_4 as the long-lived tracer are shown.

date	tracer HF	altitude range (K)	tracer CH_4	altitude range (K)	tracer HF and CH_4
March 1992	2.0±0.3	390–445	1.9±0.3	410–450	2.0±0.4
March 1993	2.2±0.3	405–460	2.2±0.2	390–460	2.2±0.2
March 1994	1.4±0.2	420–460	1.4±0.3	400–475	1.4±0.3
March 1995	2.3±0.4	420–470	2.5±0.4	410–460	2.4±0.5
March 1996	2.2±0.1	455–515	2.6±0.3	450–500	2.4±0.5
March 1997	2.5±0.2	460–485	2.5±0.2	460–485	2.5±0.2
March 1998	1.5±0.3	410–455	1.4±0.4	430–510	1.5±0.5
March 1999	0.8±0.2	400–480	1.2±0.2	395–415	1.0±0.2
March 2000	2.4±0.1	430–455	2.5±0.1	410–455	2.5±0.2
February 2001	1.7±0.3	475–535	1.7±0.4	490–515	1.7±0.4
March 2002	0.5±0.2	380–540	0.3±0.2	380–540	0.4±0.3
February 2003	1.3±0.1	430–465	1.4±0.2	410–465	1.4±0.2

ACPD
4, 2167–2238, 2004

Table 5. Column ozone loss (DU) in 380–550 K derived for profiles inside the entire vortex and the vortex core for different months and years (Column 1), using HF (Column 2 and 3) and CH_4 as the long-lived tracer (Column 4 and 5). The error was derived from the uncertainty of the early winter reference function and the standard deviation σ of the result is shown in brackets. No standard deviation is shown if the column ozone loss had to be calculated from only one profile.

date	HF: entire (σ)	HF: core (σ)	CH_4: entire (σ)	CH_4: core (σ)
1992				
February	66±18	66±18	68±17	68±17
March	71±17 (36)	85±17 (30)	58±16 (32)	71±16 (24)
April	77±19 (11)	73±19 (12)	83±19 (15)	83±18 (15)
1993				
March	90±25 (25)	104±24 (11)	93±17 (38)	109±17 (27)
April	89±26 (33)	100±25 (21)	104±18 (30)	117± 17 (23)
1994				
February	16±19 (21)		4±23 (30)	
March	40±17 (17)	48±16 (11)	28±21 (22)	37±20 (16)
April	44±19 (19)	41±19 (20)	57±23 (18)	56±23 (16)
1995				
March	79±24 (28)	84±24 (21)	79±24 (27)	83±23 (22)
April	63±27 (23)	62±27 (23)	76±26 (19)	75±26 (19)
1996				
March	81±9 (20)	82±9 (19)	102±22 (24)	102±22 (24)

ACPD
4, 2167–2238, 2004

Table 5. Continued.

date	HF: entire (σ)	HF: core (σ)	CH_4: entire (σ)	CH_4: core (σ)
April	84±8 (18)	87±8 (13)	116±20 (20)	119±20 (14)
1997				
March	41±21 (25)	52±20 (21)	42±20 (31)	56±20 (26)
April	42±21 (29)	61±20 (24)	38±20 (36)	59±19 (28)
May	69±19 (40)		74±18 (40)	
1998				
March	48±21 (21)	50±21 (17)	43±33 (21)	47±32 (20)
1999				
February	28±13 (9)	26±13 (8)	30±8 (20)	28±8 (23)
March	21±14 (8)	15±13 (4)	40±8 (16)	38±7 (28)
2000				
February	35±7 (19)	42±7 (7)	41±16 (33)	52±16 (8)
March	63±7 (27)	83±6 (13)	73±15 (26)	89±15 (17)
April	78±8 (7)		79±19 (19)	
2002				
March	12±10 (4)	5±10 (9)	-5±13 (13)	0±13 (9)
April	16±13 (9)	14±13 (13)	3±16 (7)	2±17 (8)
2003				
January	23 ±9 (14)		53 ±11 (19)	
February	37±9 (12)	51±9 (6)	66 ±12 (13)	81±12 (8)
April	44±10 (11)	49±10 (11)	71±13 (6)	74±13 (5)

ACPD
4, 2167–2238, 2004

Table 6. Column ozone loss (DU) in the altitude range of 400–500 K (450–500 K in 2000–2001) derived for profiles inside the entire vortex and the vortex core for different month and years (Column 1), using HF (Column 2 and 3) and CH_4 as the long-lived tracer (Column 4 and 5). The error was derived from the uncertainty of the early winter reference function and the standard deviation σ of the result is shown in brackets. No standard deviation is shown if the column ozone loss had to be calculated from only one profile.

date	HF: entire (σ)	HF: core (σ)	CH_4: entire (σ)	CH_4: core (σ)
1992				
February	50±11	50±11	53±11	53±11
March	54±11 (21)	60±11 (20)	48±10 (21)	55±10 (19)
April	53±12 (7)	53±12 (6)	59±11 (6)	60±11 (5)
1993				
March	68±15 (18)	77±15 (5)	67±10 (21)	78±10 (10)
April	67±16 (22)	73±16 (13)	74±11 (18)	82±10 (11)
1994				
February	11±11 (17)		6±14 (25)	
March	27±10 (14)	34±10 (8)	21±13 (17)	27±13 (12)
April	31±12 (13)	30±12 (12)	42±14 (12)	41±14 (10)
1995				
March	61±14 (20)	65±15 (14)	61±14 (18)	64±14 (13)
April	33±16 (14)	52±16 (13)	62±15 (14)	62±15 (14)
1996				
March	62±6 (19)	62±6 (19)	78±14 (20)	78±14 (20)
April	64±5 (14)	66±5 (10)	88±13 (16)	91±12 (11)
1997				

ACPD
4, 2167–2238, 2004

Table 6. Continued.

date	HF: entire (σ)	HF: core (σ)	CH_4: entire (σ)	CH_4: core (σ)
March	31±13 (21)	40±13 (18)	35±13 (26)	46±12 (22)
April	30±13 (24)	47±13 (20)	30±13 (29)	47±12 (22)
May	46±12 (32)		50±11 (34)	
1998				
March	39±13 (15)	42±13 (14)	36±20 (18)	37±20 (16)
1999				
February	21±8 (6)	20±8 (7)	24±5 (19)	22±5 (17)
March	19±9 (8)	13±8 (8)	31±5 (8)	28±5 (14)
2000				
February	27±5 (18)	42±7 (7)	30±10 (22)	35±10 (3)
March	50±4 (22)	67±4 (10)	55±9 (22)	67±9 (12)
April	77±5 (5)		80±11 (2)	
2001				
February	10±5 (9)	8±5	11±7 (8)	6±6
2002				
March	1±7 (7)	5±6 (5)	-6±8 (10)	-2±8 (8)
April	10±8 (5)	10±8 (4)	4±10 (5)	4±10 (5)
2003				
January	21 ±5 (13)		37 ±7 (13)	
February	32±6 (11)	43±6 (5)	47 ±7 (6)	57±7 (5)
April	34±6 (9)	37±6 (5)	52±7 (5)	55±8 (5)

ACPD
4, 2167–2238, 2004

Table 7. Calculated chemical loss in column ozone loss in the Arctic in winters 1993–1994 to 2001–2002. Comparison between HALOE results and results from other methods.

date	SAOZ/ REPROBUS [%] in 380–600 K	SAOZ/ REPROBUS [DU] in 370–700 K	Match [DU] in 380–550 K	HALOE [DU] entire vortex in 380–550 K	HALOE [DU] vortex core
Jan–Mar 1994	7	31		34±23	43±22
mid-Jan–Mar 1995	21	95	108±18	77±27	82±27
mid-Jan–Mar 1996	20	83		92±25	93±25
Jan–Mar 1997	22	110		46±22	61±22
Jan–Mar 1998	12	57		46±35	49±33
Dec–Mar 1999	5	25		31±24	27±24
Dec–Mar 2000	23	105		68±12	86±15
Jan–Apr 2002	7	32		10±21	8±20

ACPD
4, 2167–2238, 2004

Table 8. Calculated chemical loss in column ozone loss (DU) in the Arctic over seven winters, HALOE results and MLS results (Manney et al., 2003a), are compared.

date	MLS[a] above 100 hPa	HALOE entire vortex in 400–550 K	HALOE vortex core in 400–550 K
March 1992	29	56±15	62±15
March 1993	54	78±19	89±19
March 1994	35	29±18	37±16
March 1995	36	67±18	71±19
March 1996	63	83±20	84±20
March 1997	35	38±16	50±17
February 1998	22	45±25	47±25

[a] taken from Manney et al. (2003a), Table 3

ACPD
4, 2167–2238, 2004

Table 9. Accumulated ozone loss estimated by MLS over the calculation period in 465 K and 520 K taken from Manney et al. (2003a), Tables 1 and 2. HALOE results at 465 K and 520 K inside the vortex core were estimated from Figs. 7 and 8; in February 1997 no HALOE observations are available and, therefore, no ozone loss could be derived for February.

date	ozone loss 465 K (MLS)	ozone loss 465 (HALOE)	ozone loss 520 K (MLS)	ozone loss 520 K (HALOE)
March 1992	0.5	1.4	0.3	0.6
March 1993	1.0	2.0	0.7	0.9
March 1994	0.5	1.4	0.7	1.0
March 1995	0.8	2.0	0.2	0.8
March 1996	1.3	2.2	1.4	1.6
February 1997	0.5		0.9	
February 1998	0.4	1.3	0.02	0.6

ACPD
4, 2167–2238, 2004

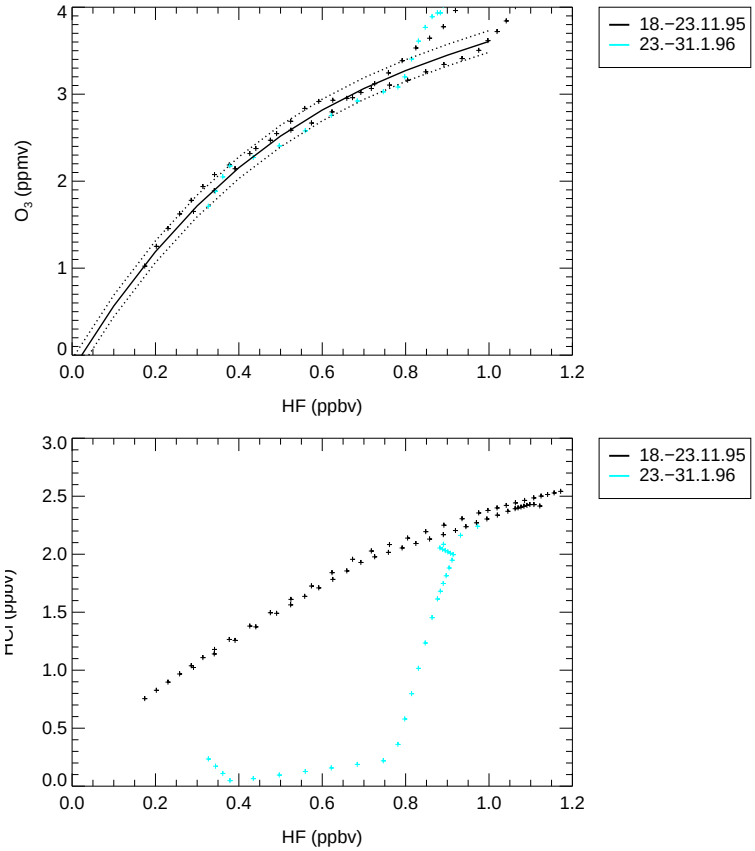

Fig. 1. Tracer-tracer profiles inside the outer early vortex of the year 1995–1996 from HALOE measurements with HF as the passive tracer. In the top panel, the chemical active tracer is O_3 and in the bottom panel the chemical active tracer is HCl. The early winter reference function for the O_3/HF relation 1995–1996, top panel, is indicated as a black solid line and the uncertainty of the reference function is represented by black dotted lines.

ACPD
4, 2167–2238, 2004

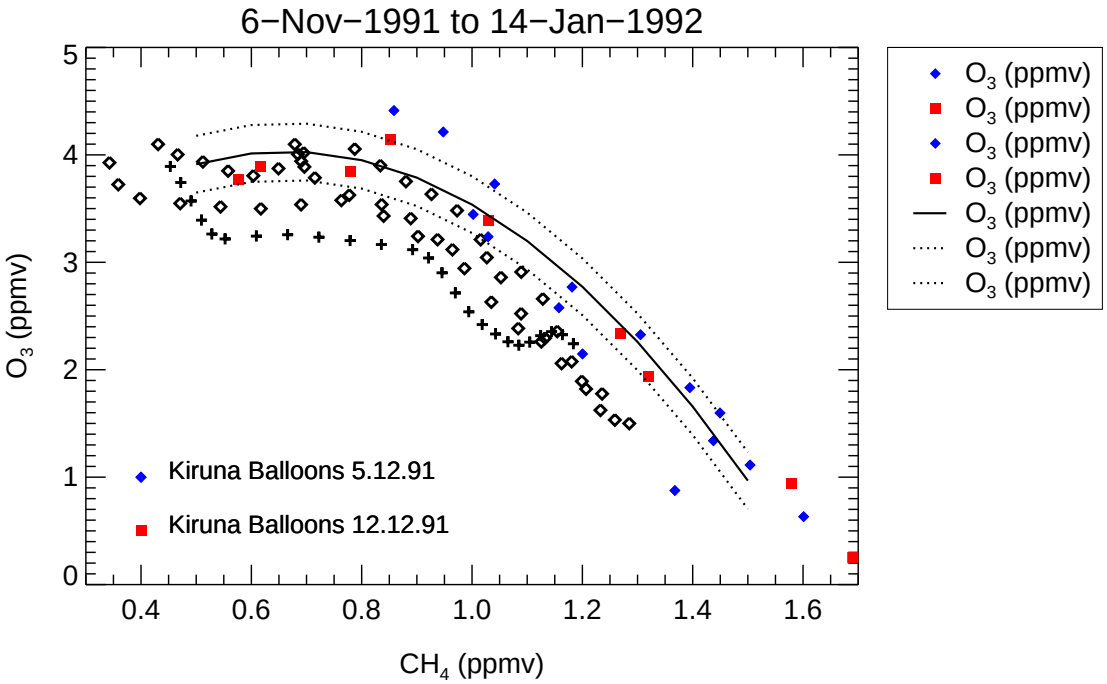

Fig. 2. The early winter reference function 1991–1992 shown as a black line was derived from balloon measurements from December 1991 (coloured symbols). Dotted lines indicate the range of uncertainty in the reference function. Observations made by HALOE within the vortex in November 1991 (black asterisks) and in January (black squares) are also shown.

ACPD
4, 2167–2238, 2004

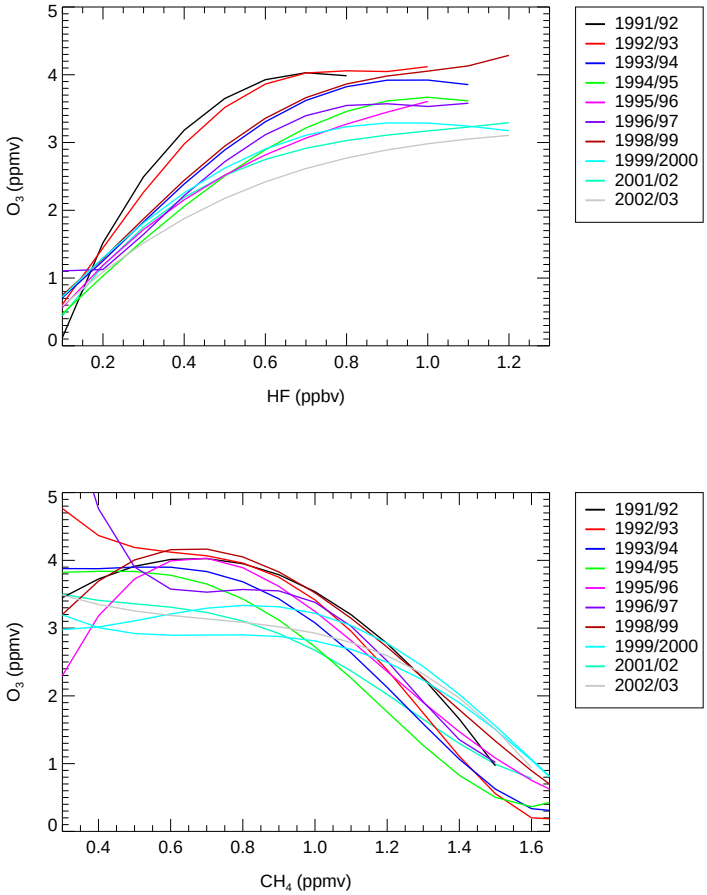

Fig. 3. Early winter reference relations for the ten years between 1991–1992 to 2002–2003 are indicated as coloured lines. O_3/HF is shown in the top panel and O_3/CH_4 is shown in the bottom panel.

ACPD
4, 2167–2238, 2004

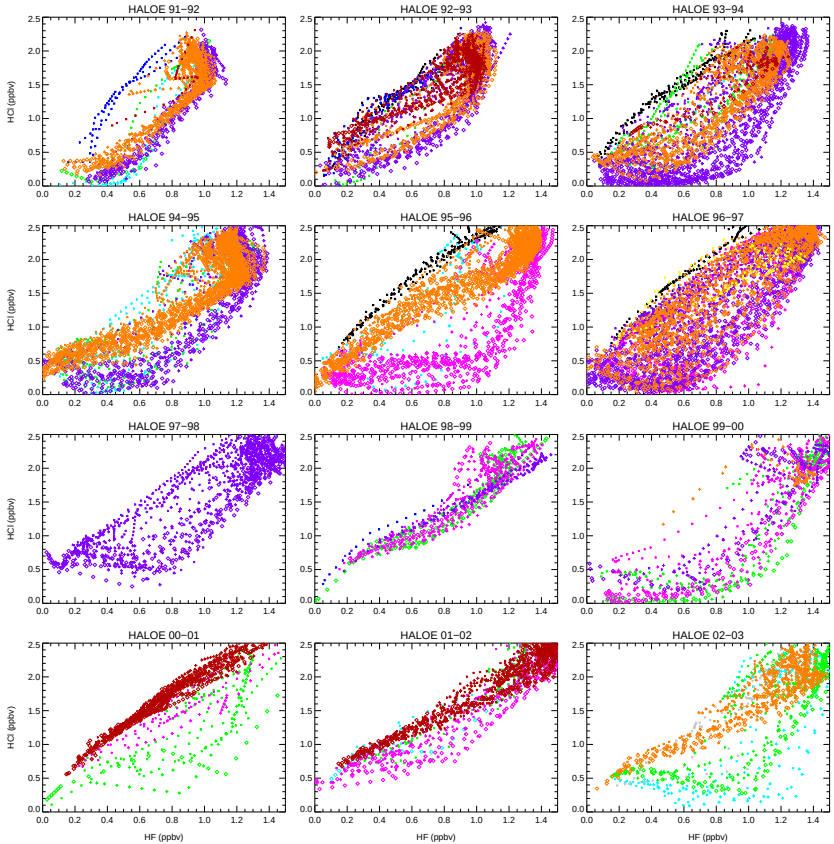

Fig. 4. HCl/HF relations for the twelve winters between 1991–1992 and 2002–2003 as measured from profiles inside the vortex core (diamonds), inside the outer vortex (large plus signs), inside an outer part of the outer vortex (small crosses) by HALOE are shown. Different colours of profiles indicate the different time intervals when profiles were observed: November (black), December (blue), January (cyan), February (green), first part of March (magenta), second part of March (purple), first part of April (orange), second part of April (dark red).

ACPD
4, 2167–2238, 2004

Ozone loss and chlorine activation in the Arctic winters 1991–2003

S. Tilmes et al.

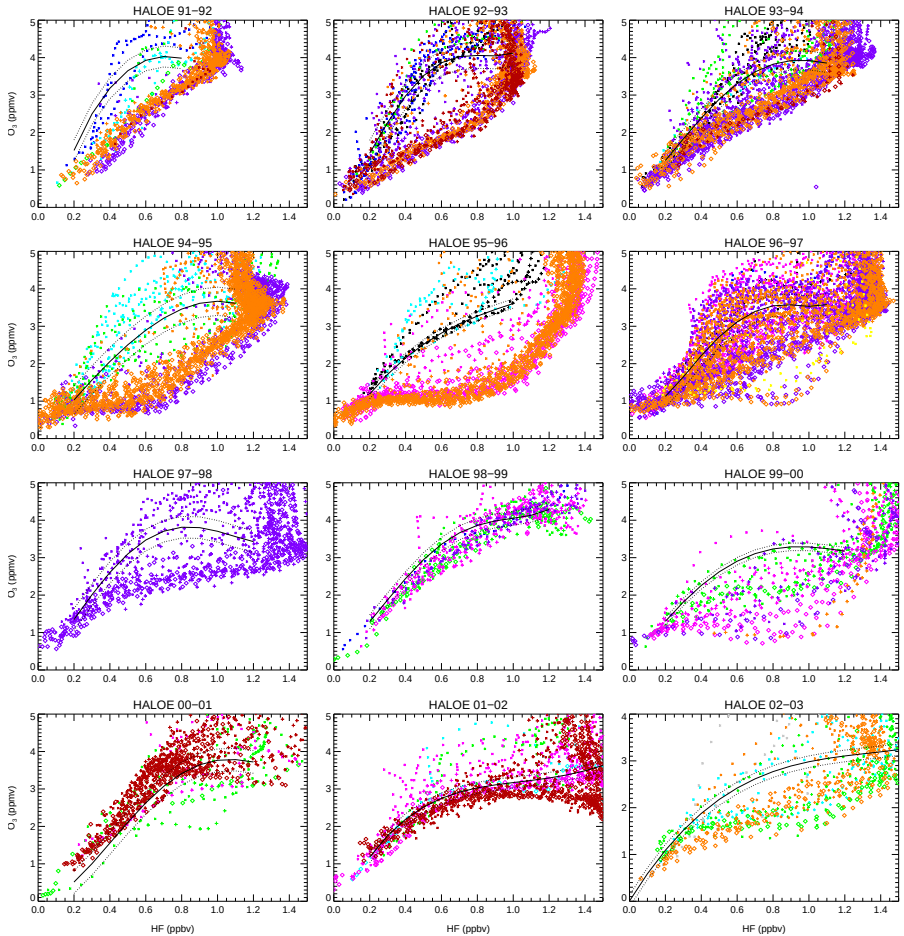

Fig. 5. As Fig. 4 but O_3/HF relations.

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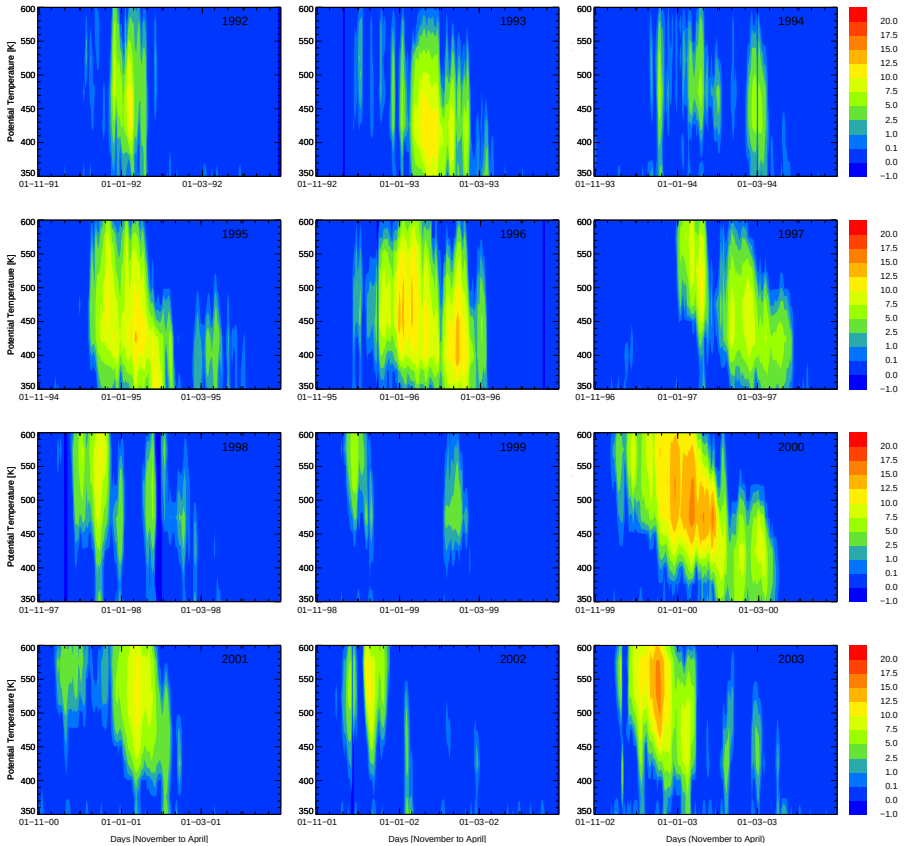

Fig. 6. The area of possible PSC existence in 10^6 km^2 over the entire polar vortex, as a function of altitude, is shown for the time period from November to April for the twelve winters between 1991–1992 and 2002–2003. The PSC threshold temperature was calculated with the analysed UKMO temperatures and pressures assuming typical stratospheric mixing ratios of HNO_3 (10 ppbv) and H_2O (5 ppmv) (Hanson and Mauersberger, 1988).

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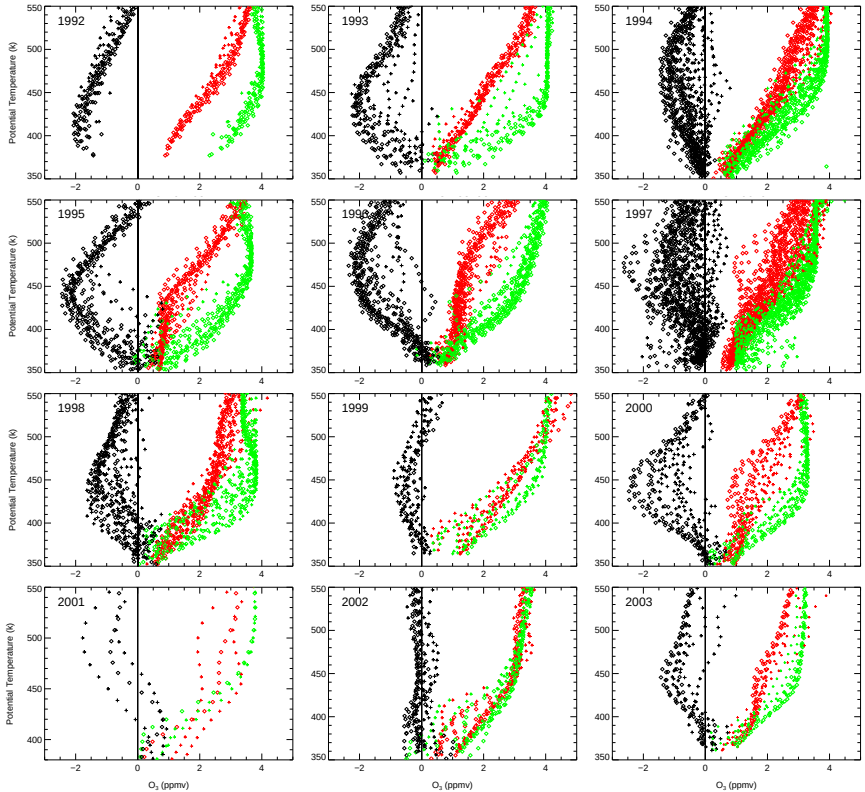

Fig. 7. Vertical profiles (plotted against potential temperature) of measured O_3 mixing ratios (red diamonds) by HALOE, the ozone mixing ratios expected in the absence of chemical change ($\hat{O}_3$, green diamonds), and the difference between expected and observed O_3 (ΔO_3, black diamonds) are shown for the winters between 1991–1992 and 2001-2002 in March (2000–2001, 2002–2003 in February). $\hat{O}_3$ was inferred using HF as the long-lived tracer and the early winter reference functions (Table 2), from profiles inside the vortex core (squares) and inside the outer vortex (plus signs).

ACPD
4, 2167–2238, 2004

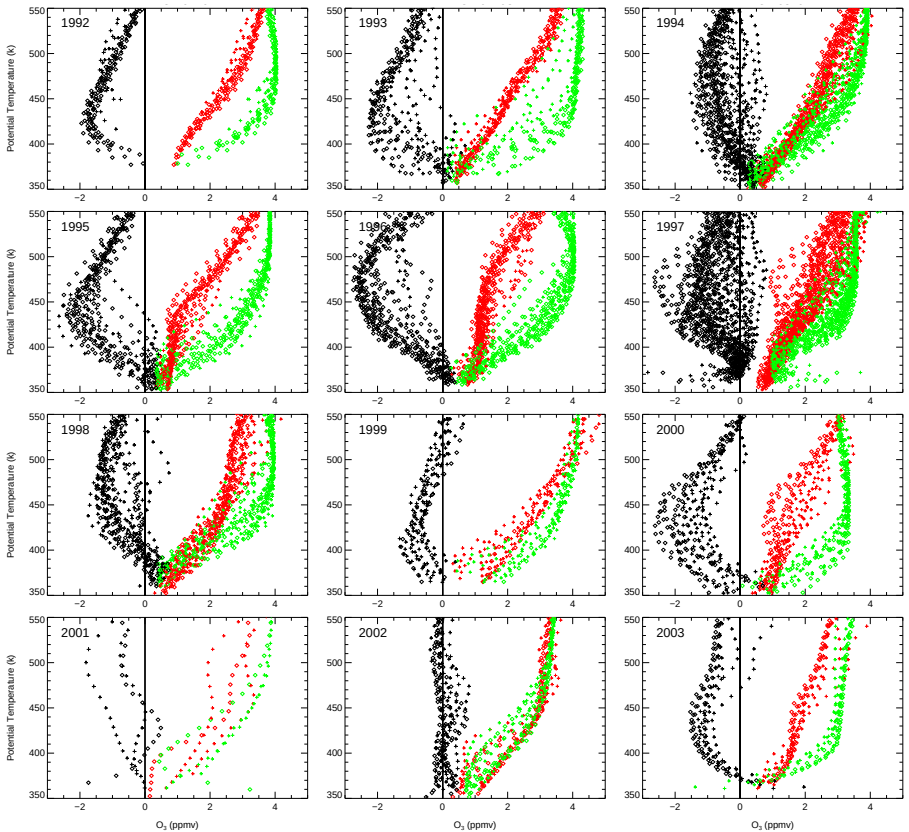

Fig. 8. As in Fig. 7, but with CH_4 used as the long-lived tracer and the early winter reference functions (Table 3).

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4, 2167–2238, 2004

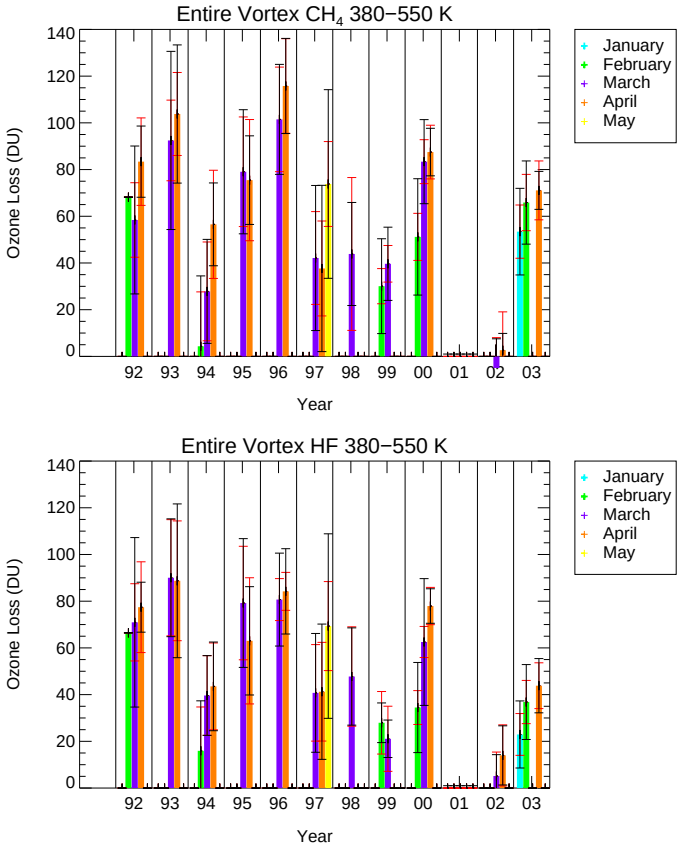

Fig. 9. Monthly averaged column ozone loss derived for profiles inside the entire vortex in 380–550 K, February (green), March (purple), April (orange) and May (yellow) in winters between 1991–1992 and 2002–2003. The red error bar indicates the uncertainty of the early winter reference function, the black error bar the standard deviation. Top panel: CH_4 was used as the long-lived tracer, bottom panel: HF was used as the long-lived tracer. Ozone loss was derived from profiles inside the entire vortex.

ACPD
4, 2167–2238, 2004

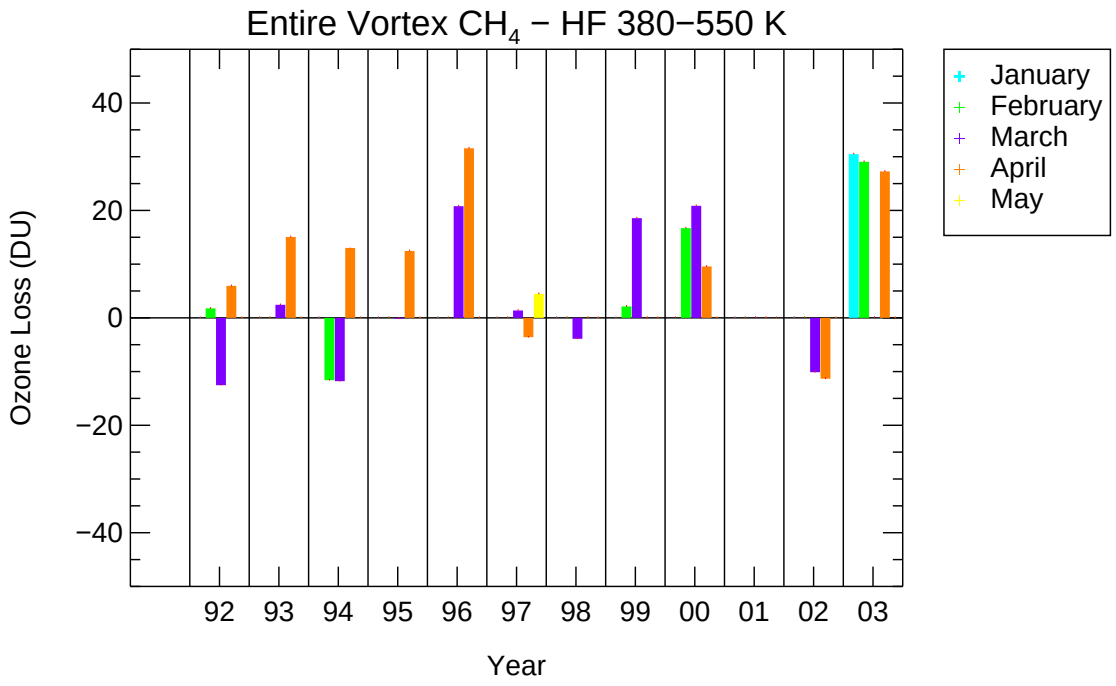

Fig. 10. Difference between monthly averaged column ozone loss derived for profiles inside the entire vortex in 380–500 K using HF and CH_4 as the long-lived tracer (see Fig. 9 top and bottom panel). Ozone loss was derived from profiles inside the entire vortex.

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4, 2167–2238, 2004

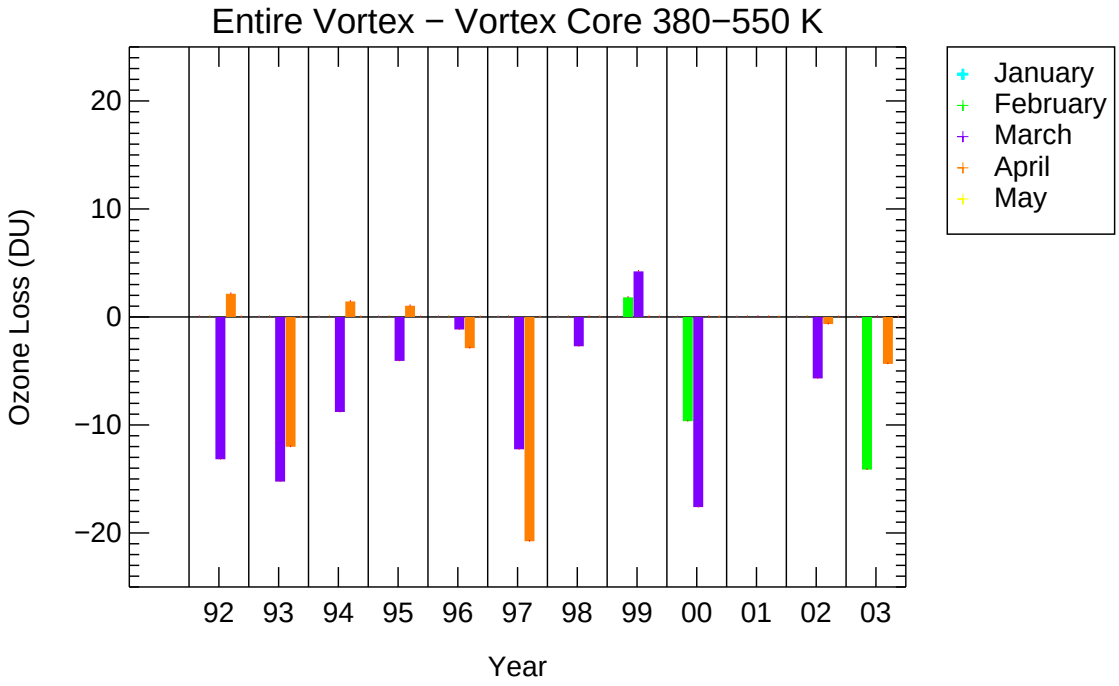

Fig. 11. Difference of monthly averaged column ozone loss between the entire vortex and the vortex core for all winters between 1991–1992 and 2002–2003, using both CH_4 and HF as the long-lived tracers. Results were derived in an altitude range of 380–550 K.

ACPD
4, 2167–2238, 2004

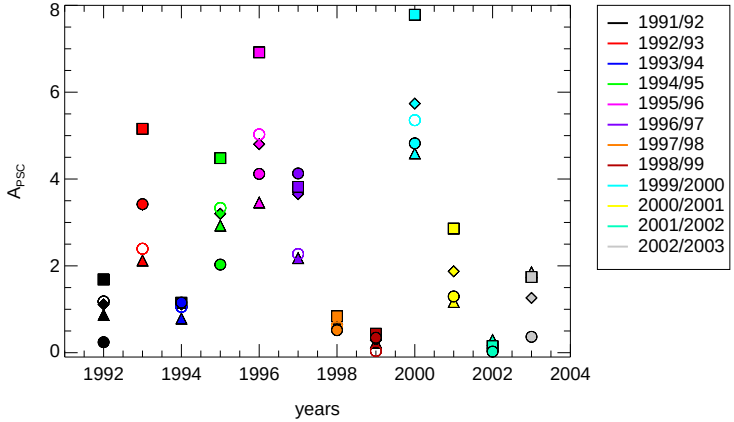

Fig. 12. Daily mean A_{PSC} in 10^6 km^2 averaged between 400–500 K in the Arctic polar vortex using UKMO data, for the years 1991–1992 to 2002–2003 in different colours. Different symbols indicate different time intervals to calculate the averaged daily mean A_{PSC}: filled-square: January–February; filled diamond: January–March; filled triangle: December–April; filled circle: mid-January–March; open circle: mid-January–March (pers. comm. M. Rex, 2003).

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4, 2167–2238, 2004

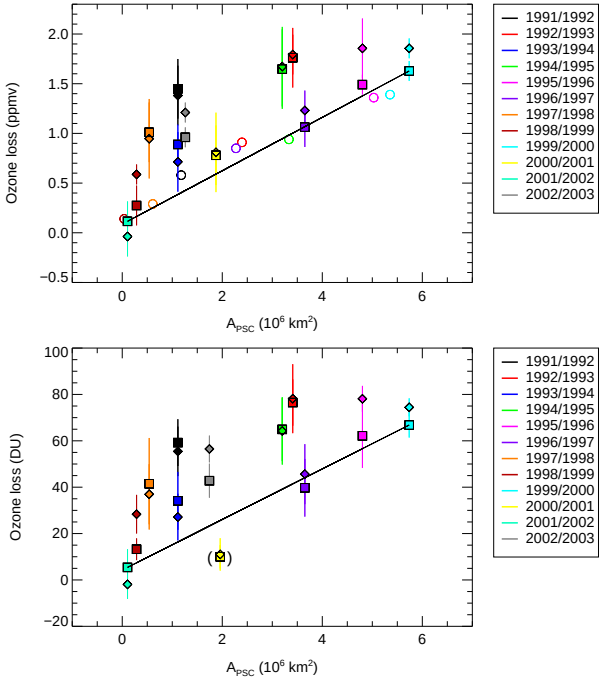

Fig. 13. Top panel: relation between the accumulated ozone loss in mixing ratio and A_{PSC} in the Arctic polar vortex for the years 1991–1992 to 2002–2003 in different colours. Monthly averaged ozone loss inside the vortex core in March (February in 2000–2001 and 2002–2003) between 400–500 K (between 450–500 K inside the entire vortex in winter 2000–2001), using the TRAC method, coloured solid squares (HF is used as the long-lived tracer) and solid diamonds (CH_4 is used as the long-lived tracer). A_{PSC} was averaged between January to March of each year and between 400–500 K derived from UKMO data. Ozone loss derived with the average approach (Rex et al., 2002) is shown in coloured open circles and A_{PSC} using ECMWF data. Black line indicates a linear relation between A_{PSC} and ozone loss. Bottom panel: as top panel, but for the column ozone loss (DU) in the altitude range 400–500 K derived only from HALOE observations is apparent.

ACPD
4, 2167–2238, 2004

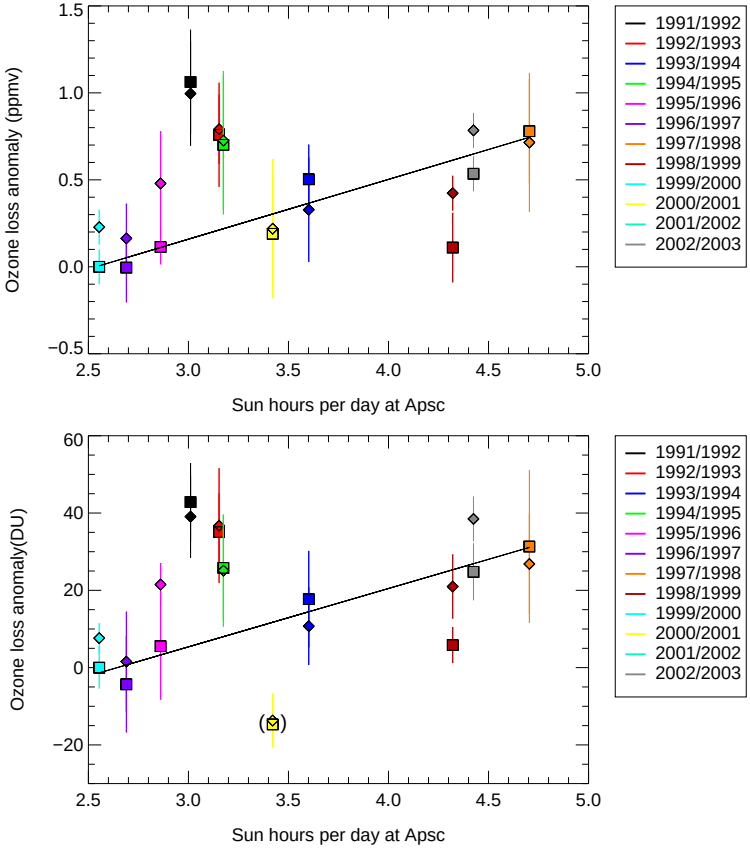

Fig. 14. Top panel: deviation of accumulated ozone loss in mixing ratio from the linear relation (black line in Fig. 13, top panel), in relation to sun hours per day at (A_{PSC}) (see text). Bottom panel: deviation of column ozone loss (DU) from the linear relation (black line in Fig. 13, bottom panel), in relation to sun hours per day at (A_{PSC}) (see text).

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